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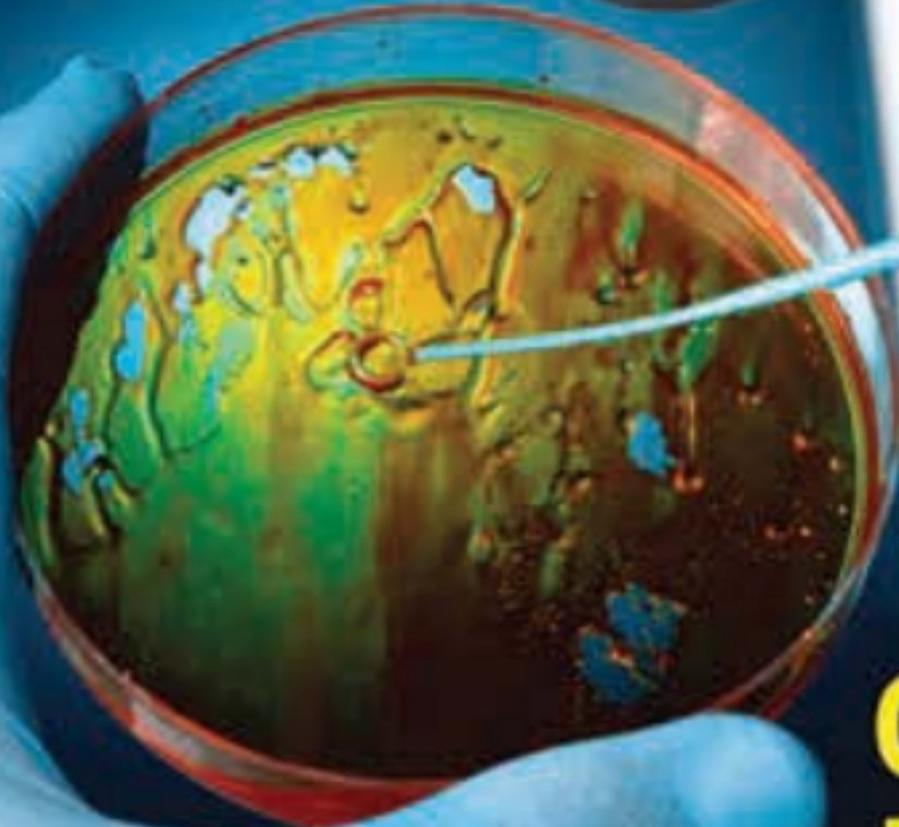
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The Status of Chemistry and Chemical Engineering in India

One has Pure Chemistry, Applied Chemistry, Chemical Engineering, Nuclear Chemistry, etc. Chromatography or Spectroscopy can both be called brothers. But spectroscopy— γ -ray, X-ray, ultraviolet, visible are the big brothers in the methods of analysis. The standard of spectroscopic analysis followed in India is second to none. Spectrometers are also part of the pack of instruments sent to Mars. The standard of chemistry laboratories is quite high, as good as any other discipline. Our advice to our young friends is this – whatever may be your subject, go as deep as you can, compare this with other methods and then try to see how your own results can be improved by combining your work with other methods.

The periodic table of elements is the first attempt to sanity and order in the study of elements. These properties were then related to the atomic numbers. These were related to the nucleus and the peripheral electrons, with protons and neutrons playing their part. Isotopes were discovered. One can go on with this gripping story. This will be more exciting than reading James Bond.

There is no laboratory connected with Nuclear Chemistry, Metallurgy, Minerals and Precious stones, Cotton, Silk and their imitations. The rush for science in colleges is not because science is more paying. It is only because it is very interesting as well as exciting as one goes from one chapter to another. That is the driving force for the scientists to go on working. This makes life worth-living. Wishing you all the best.

Anil Ahlawat
Editor

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CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

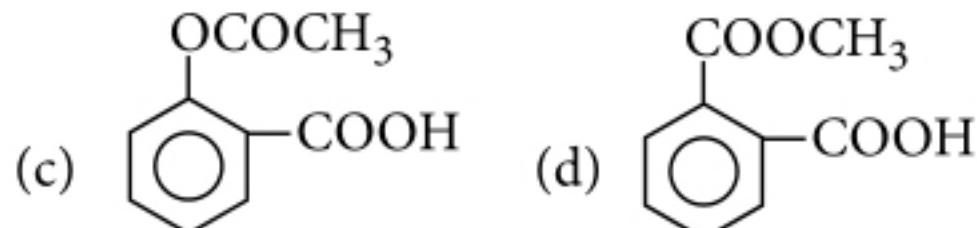
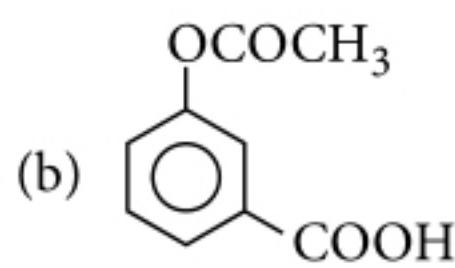
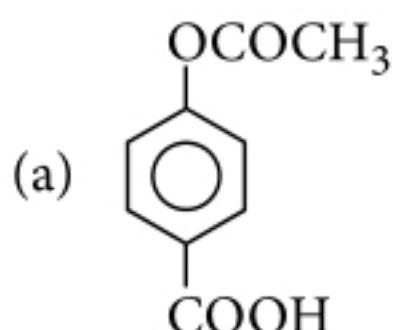
The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 16

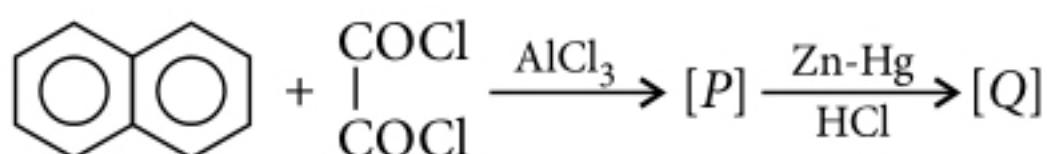
JEE MAIN/PMTs

1. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (also known as blue vitriol) is often added to swimming pools to kill algae. It is prepared by the reaction between copper metal and hot sulphuric acid to give $\text{CuSO}_{4(aq)}$ and $\text{SO}_{2(g)}$. Molecules of $\text{SO}_{2(g)}$ obtained when one mole of copper is reacted with one mole of sulphuric acid are
(a) 3.0×10^{23} (b) 6.023×10^{23}
(c) 3.0×10^{24} (d) $64 \times 6.023 \times 10^{23}$
2. Which of the following is a redox reaction?
(a) $2\text{CuSO}_4 + 4\text{KI} \rightarrow \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$
(b) $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$
(c) $\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow \text{BaSO}_4 + 2\text{NaCl}$
(d) $\text{CuSO}_4 + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
3. An organic compound 'A' having vapour density 47, gives characteristic colour with FeCl_3 . 'A' when treated with CO_2 and NaOH at 140°C under pressure gives 'B' which on being acidified gives 'C'. It reacts with acetyl chloride to give 'D', a pain killer. The structure of 'D' is



4. The equilibrium constant for the reaction $\text{OCl}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{HOCl}_{(aq)} + \text{OH}_{(aq)}^-$ is 3.6×10^{-7} . Hence, K_a for HOCl is
(a) 2.8×10^{-8} (b) 3.6×10^{-7}
(c) 6.0×10^{-1} (d) 2.8×10^6

5. In the following reaction sequence,



Q is

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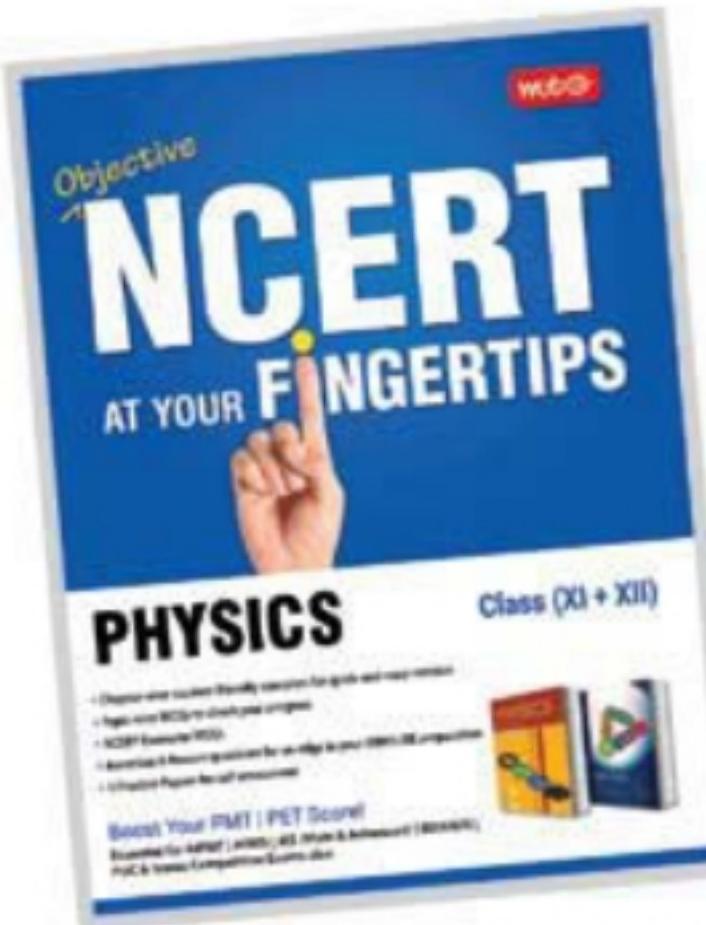
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2. Patil Basu
3. Suraj Chatterjee, Kolkata (West Bengal)

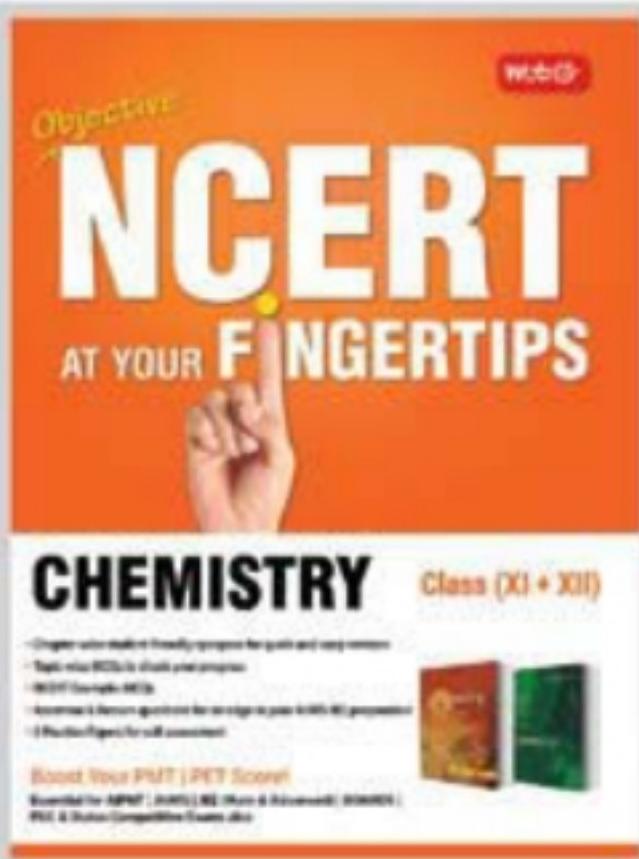
SET 14

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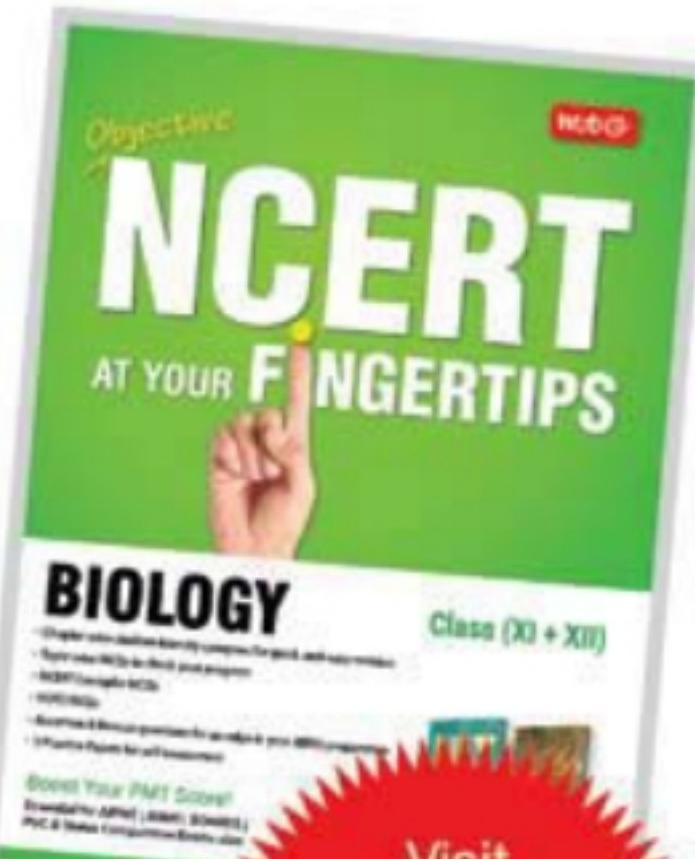
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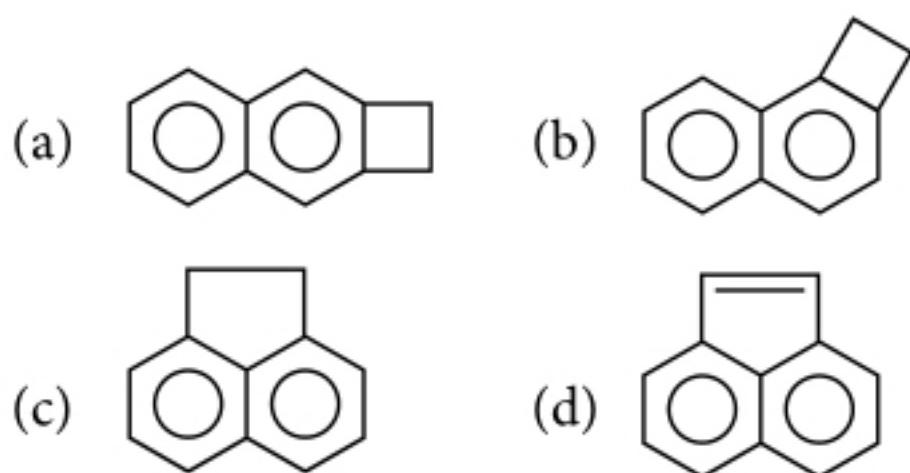


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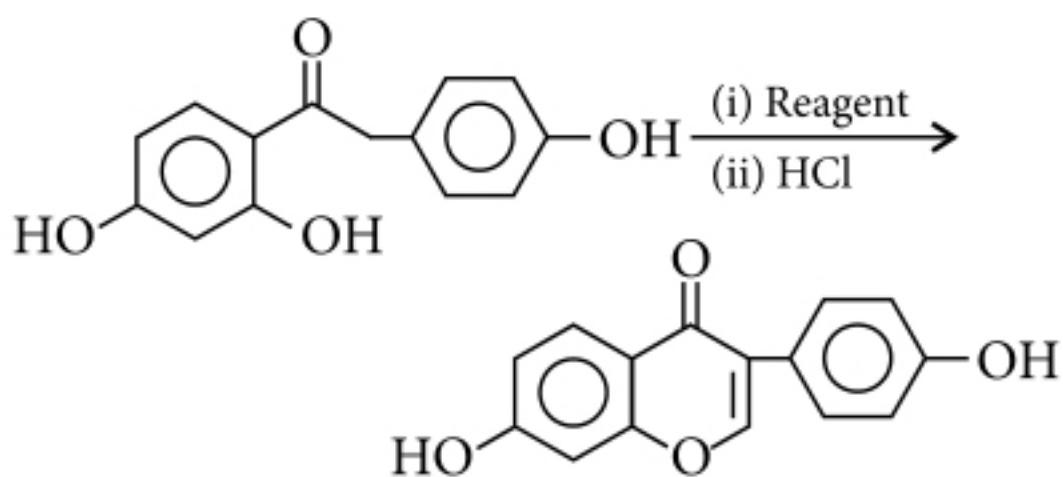
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JEE ADVANCED

6. Identify the reagent in the given reaction.



- (a) HCHO, $\text{C}_2\text{H}_5\text{ONa}$
 (b) CH_3CHO , OH^-
 (c) HCOOC_2H_5
 (d) HCOOC_2H_5 , $\text{C}_2\text{H}_5\text{ONa}$

COMPREHENSION

On the basis of elemental analysis, the empirical formula as also molecular formula of a chromium complex was found to be $\text{CrN}_4\text{H}_{12}\text{Cl}_2\text{Br}$. This complex could be isolated in two isomeric forms. One of these two forms was found to produce a white precipitate on reaction with AgNO_3 solution. The white precipitate was found to be readily soluble in dilute aqueous ammonia. The other isomer forms a yellow precipitate on reaction with AgNO_3 and this yellow precipitate is only partly soluble in concentrated ammonia solution.

7. If we measure the conductivity of aqueous solutions of these two isomers, the conductivity of the isomer forming white ppt. with AgNO_3 and that forming yellow ppt. will be found to be as follows :
 (a) conductivity of isomer forming white precipitate with AgNO_3 is more than that of the other

- (b) conductivity of isomer forming yellow precipitate with AgNO_3 will be more than the other
 (c) conductivity of both the isomers will be same
 (d) none of the above is correct.

8. In the two isomers,

- (a) the oxidation state of Cr is +2
 (b) the number of unpaired electrons is 3
 (c) the number of unpaired electrons is 2
 (d) In one, there are two unpaired electrons whereas in the other, there are three unpaired electrons.

INTEGER VALUE

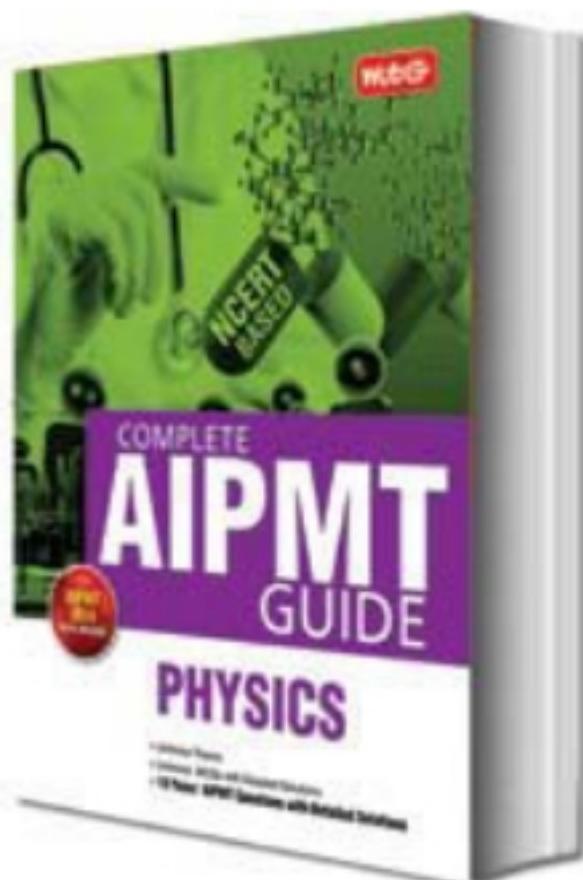
9. Pure water has reversible reduction potential of -0.413 V under 1.00 atm H_2 pressure. If $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$ is considered to be the reduction, then pH of pure water is
 10. The value of n in the molecular formula $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18}$ is

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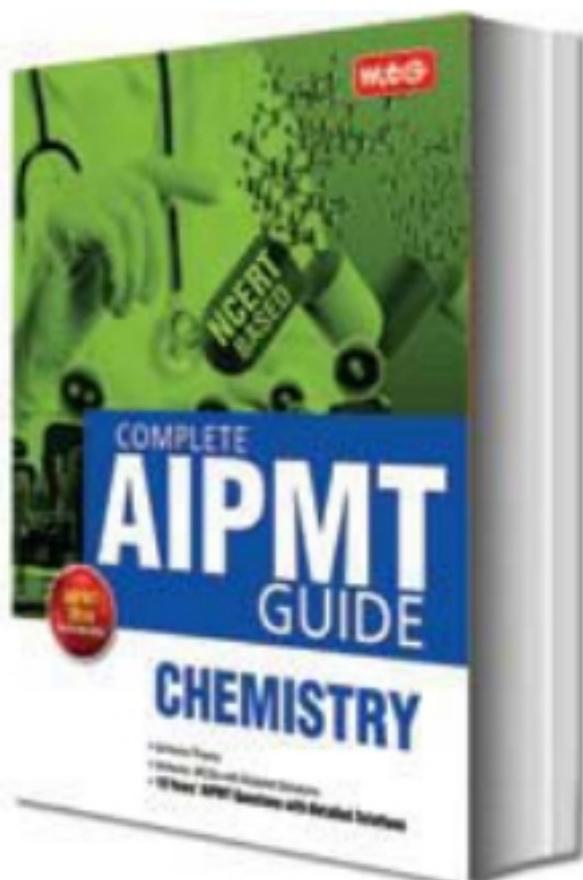
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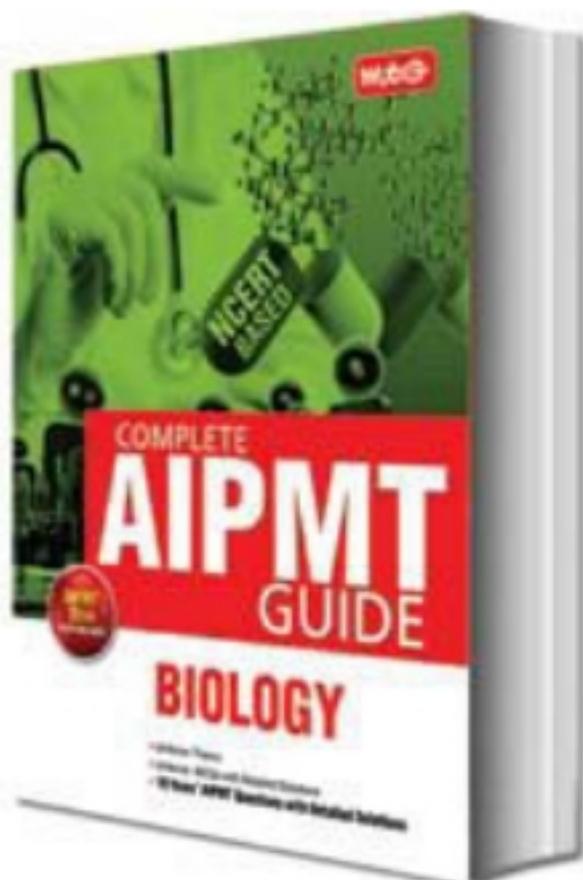
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HIGHLIGHTS:

- 100% NCERT based
- Comprehensive unitwise theory complemented with concept maps, flowcharts and easy-to-understand illustrations
- Last 10 years' questions (2005-2014) of AIPMT
- Unit-wise MCQs with detailed explanations and solutions
- Over 50% of questions that appeared in AIPMT 2014 were from MTG's Complete AIPMT Guides



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EXAMINER'S MIND NCERT

CLASS XI

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced) / AIPMT / AIIMS/other PMTs have drawn their papers heavily from NCERT books.

THE p-BLOCK ELEMENTS (Group 13 and 14) | ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

SECTION - I

Only One Option Correct Type

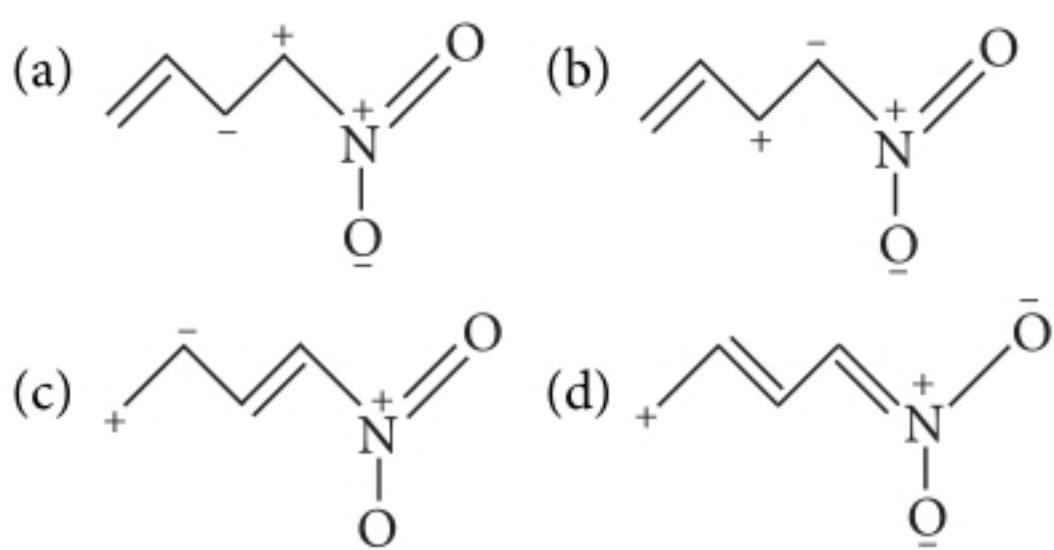
This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. When chlorine is passed through molten tin, the product obtained is
(a) SnCl_4 (b) $[\text{SnCl}_6]^{2-}$
(c) $[\text{SnCl}_4]^{2-}$ (d) SnCl_2
2. Select the incorrect statement.
(a) $\overset{+}{\text{CH}_3}$ is called carbanion.
(b) In $\overset{+}{\text{CH}_3}$, carbon is even more electron deficient than that in a radical.
(c) In $\overset{+}{\text{CH}_3}$, the vacant *p*-orbital is perpendicular to the plane of C—H bond.
(d) $\overset{+}{\text{CH}_3\text{CH}_2}$ is called carbenium ion.
3. 2 g of aluminium is treated separately with excess of dilute H_2SO_4 and excess of NaOH. The ratio of the volumes of hydrogen evolved is
(a) 2 : 3 (b) 1 : 1
(c) 2 : 1 (d) 1 : 2
4. Which is the incorrect name of CH_3NC ?
(a) Acetoisonitrile
(b) Methyl isocyanide
(c) Methyl carbylamine
(d) Methyl isonitrile
5. Group 13 elements show +1 and +3 oxidation states. Relative stability of +3 oxidation state may be given as

- (a) $\text{Tl}^{3+} > \text{In}^{3+} > \text{Ga}^{3+} > \text{Al}^{3+} > \text{B}^{3+}$
(b) $\text{B}^{3+} > \text{Al}^{3+} > \text{Ga}^{3+} > \text{In}^{3+} > \text{Tl}^{3+}$
(c) $\text{Al}^{3+} > \text{Ga}^{3+} > \text{Tl}^{3+} > \text{In}^{3+} > \text{B}^{3+}$
(d) $\text{Al}^{3+} > \text{B}^{3+} > \text{Ga}^{3+} > \text{Tl}^{3+} > \text{In}^{3+}$
6. The presence of carbon in an organic compound can be shown by
(a) heating the compound with sodium
(b) heating the compound with cupric oxide
(c) heating the compound on bunsen flame
(d) heating the compound with magnesium.
7. Orthoboric acid contains
(a) pyramidal BO_3^{3-} units
(b) linear BO_3^{3-} units
(c) T-shaped BO_3^{3-} units
(d) triangular BO_3^{3-} units.
8. What is the correct order of decreasing stability of the following cations?
$$\text{CH}_3-\overset{+}{\text{CH}}-\text{CH}_3$$
 $\text{CH}_3-\overset{+}{\text{CH}}-\text{OCH}_3$
$$\text{CH}_3-\overset{+}{\text{CH}}-\text{CH}_2-\text{OCH}_3$$

(a) II > I > III (b) II > III > I
(c) III > I > II (d) I > II > III
9. Wood charcoal is used in gas masks because it
(a) is poisonous (b) liquefies gas
(c) is porous (d) adsorbs gases.
10. The increasing order of stability of the following radicals is
(a) $(\text{CH}_3)_2\dot{\text{C}} < (\text{CH}_3)_3\dot{\text{C}} < (\text{C}_6\text{H}_5)_2\dot{\text{C}} < (\text{C}_6\text{H}_5)_3\dot{\text{C}}$
(b) $(\text{C}_6\text{H}_5)_3\dot{\text{C}} < (\text{C}_6\text{H}_5)_2\dot{\text{C}} < (\text{CH}_3)_3\dot{\text{C}} < (\text{CH}_3)_2\dot{\text{C}}$

12. Among the following, the least stable resonance structure is



13. CO behaves as

- (a) Lewis acid (b) Lewis base
 (c) amphoteric oxide (d) none of these.

14. Can homologues be isomers?

15. CCl_4 is used as a fire extinguisher because

- (a) its melting point is high
 - (b) it forms covalent bond
 - (c) its boiling point is low
 - (d) it gives incombustible va

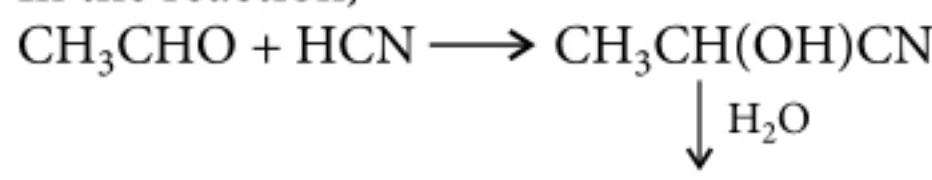
16. The attacking species in the aromatic sulphonation is

- (a) SO_3H^+ (b) H_3SO_4^+
 (c) HSO_4^- (d) SO_3

17. On passing CO_2 into aqueous solution containing Al^{3+} ions

- (a) $\text{Al}_2(\text{CO}_3)_3$ is formed
 - (b) $\text{Al}(\text{OH})_3$ is precipitated
 - (c) $[\text{Al}(\text{OH})_4]^-$ is formed
 - (d) colloidal $\text{Al}(\text{OH})_3$ is formed.

18. In the reaction,



an asymmetric centre is generated. The acid obtained would be

- (a) *D*-isomer
 - (b) *L*-isomer
 - (c) 50% *D* and 50% *L*-isomer
 - (d) 20% *D* and 80% *L*-isomer.

19. Which of the following has the highest calorific value?

- (a) Coal gas (b) Water gas
 (c) Producer gas (d) Carbon dioxide gas

20. Which of the following is isomeric with methyl vinyl ether?

- (a) 1-Propanol (b) Ethyl methyl ether
(c) Propanal (d) Ethanol

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. Which of the following statement(s) is/are correct?

- (a) Fullerenes have dangling bonds.
 - (b) Fullerenes are cage-like molecules.
 - (c) Graphite is thermodynamically most stable allotrope of carbon.
 - (d) Graphite is slippery and hard and therefore used as a dry lubricant in machines.

22. Lassaigne's extract is heated with concentrated HNO_3 before testing for halogen because
(a) silver iodide is insoluble in HNO_3

- (a) silver halide are insoluble in HNO_3
 - (b) Na_2S and NaCN are decomposed by HNO_3
 - (c) Ag_2S is soluble in HNO_3
 - (d) AgCN is soluble in HNO_3 .

23. Choose the incorrect order of relative stabilities of the given compounds.

- (a) TlI < InI < GaI
 (b) GeCl₂ > SnCl₂ > PbCl₂
 (c) GaCl₃ < InCl₃ < TlCl₃
 (d) PbI₄ > SnI₄ > GeI₄

- 24.** The correct statement(s) about the compound given below is (are)



- (a) the compound is optically active
- (b) the compound possesses centre of symmetry
- (c) the compound possesses plane of symmetry
- (d) the compound possesses axis of symmetry.

- 25.** Diborane is a Lewis acid forming addition compound $B_2H_6 \cdot 2NH_3$ with NH_3 , a Lewis base. This

- (a) is ionic and exists as $[BH_2(NH_3)_2]^+$ and $[BH_4]^-$ ions
- (b) on heating, is converted into borazine, $B_3N_3H_6$ (called inorganic benzene)
- (c) both are correct
- (d) none is correct.

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

All the elements of group 14 form tetrahalides of the general formula MX_4 which are covalent compounds (except SnF_4 and PbF_4) and have tetrahedral structures. The stability of these tetrahalides decreases as we move from C to Pb. The dihalides MX_2 of group 14 show the reverse trend. The stability of MX_2 increases as we move from C to Pb. Tetrahalides are covalent compounds while dihalides are ionic.

- 26.** Which of the following does not exist?

- (a) CCl_4
- (b) SiF_4
- (c) $PbBr_4$
- (d) $SnCl_4$

- 27.** $SiCl_4$ is easily hydrolysed but CCl_4 is not. This is because

- (a) bonding in $SiCl_4$ is ionic
- (b) silicon is non-metallic
- (c) silicon can extend its coordination number beyond four but carbon cannot
- (d) silicon can form hydrogen bonds but carbon cannot.

- 28.** Which of the following is not acidic?

- (a) PCl_3
- (b) $SbCl_3$
- (c) $BiCl_3$
- (d) CCl_4

Paragraph for Questions 29 to 31

The resonance effect is defined as 'the polarity produced in the molecule by the interaction of two π -bonds or between a π -bond and lone pair of electrons present on an adjacent atom'. The effect is transmitted through the chain.

In positive resonance effect, the transfer of electrons is away from an atom or substituent group attached to the conjugated system. This electron displacement makes certain positions in the molecule of high electron densities.

In negative resonance effect, the transfer of electrons is towards the atom or substituent group attached to the conjugated system.

- 29.** Which of the following does not show resonance effect?

- (a) 1, 3-Butadiene
- (b) Acrylonitrile
- (c) Nitrobenzene
- (d) Isopropyl isothiocyanate

- 30.** Which of the following shows $+M$ effect?

- (a) $-N(CH_3)_2$
- (b) $>C=O$
- (c) $-CN$
- (d) Both (a) and (c)

- 31.** Which of the following carboxylate ions is the most stable?

- (a) $CH_3-C(=O)-O^-$
- (b) $Cl-CH_2-C(=O)-O^-$
- (c) $F-CH_2-C(=O)-O^-$
- (d) $F\backslash CH-C(=O)-O^-$

SECTION - IV

Matching List Type

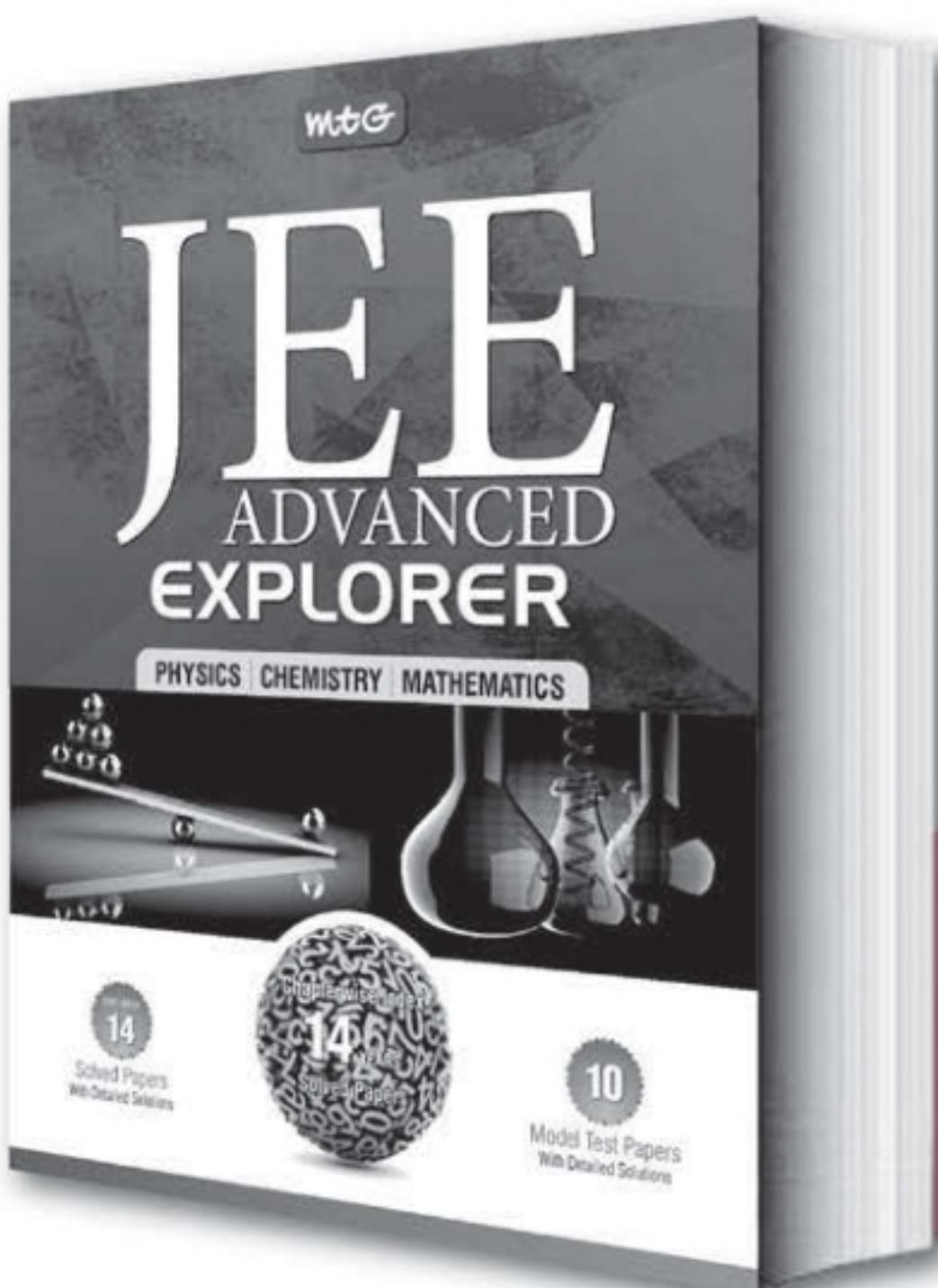
This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY one is correct.

- 32.** Match the List I with List II and select the correct answer using the code given below the lists :

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List I

- P. Shows inert pair effect
 Q. Shows $p\pi - p\pi$ back bonding
 R. Shows disproportionation reaction
 S. Shows $p\pi - d\pi$ back bonding

List II

1. InCl
 2. Ga
 3. N(SiH₃)₃

P Q R S

- (a) 4 1 3 2
 (b) 1 4 2 3
 (c) 2 4 1 3
 (d) 4 1 2 3

33. Match the List I with List II and select the correct answer using the code given below the lists :

List I

- P. Reagent used to detect phosphorus
 Q. Compound responsible for blood red colouration in Lassaigne's test
 R. Dumas method
 S. Kjeldahl's method

List II

1. [Fe(SCN)]Cl₂
 2. N₂ gas
 3. (NH₄)₂SO₄
 4. (NH₄)₂MoO₄

P Q R S

- (a) 1 2 3 4
 (b) 4 1 2 3
 (c) 4 1 3 2
 (d) 3 2 1 4

34. Match the List I with List II and select the correct answer using the code given below the lists :

List I

- P. Inductive effect
 Q. Resonance
 R. No bond resonance
 S. Electromeric effect

List II

1. Delocalisation of sigma electrons with π -bond
 2. Strong effect
 3. Permanent effect
 4. Delocalisation of π electrons

P Q R S

- (a) 3 4 1 2
 (b) 4 1 3 2
 (c) 4 3 1 2
 (d) 3 2 4 1

SECTION - V**Assertion-Reason Type**

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 (c) If assertion is true but reason is false.
 (d) If both assertion and reason are false.

35. Assertion : Silicones are water repelling in nature.

Reason : Silicones are organosilicon polymers, which have $-\text{R}_2\text{SiO}-$ as repeating unit.

36. Assertion : In steam distillation, steam is continuously bubbled through the impure organic liquid, steam heats the liquid and gets condensed.

Reason : Steam distillation is based on the difference of solubility of a given organic compound in water and in organic solvent.

37. Assertion : Hyperconjugation results in the stabilisation of carbocation by delocalising the positive charge.

Reason : Hyperconjugation produces some additional bonding between the electron-deficient carbon and the adjacent carbon.

38. Assertion : In water, orthoboric acid behaves as a weak monobasic acid.

Reason : In water, orthoboric acid acts as a proton donor.

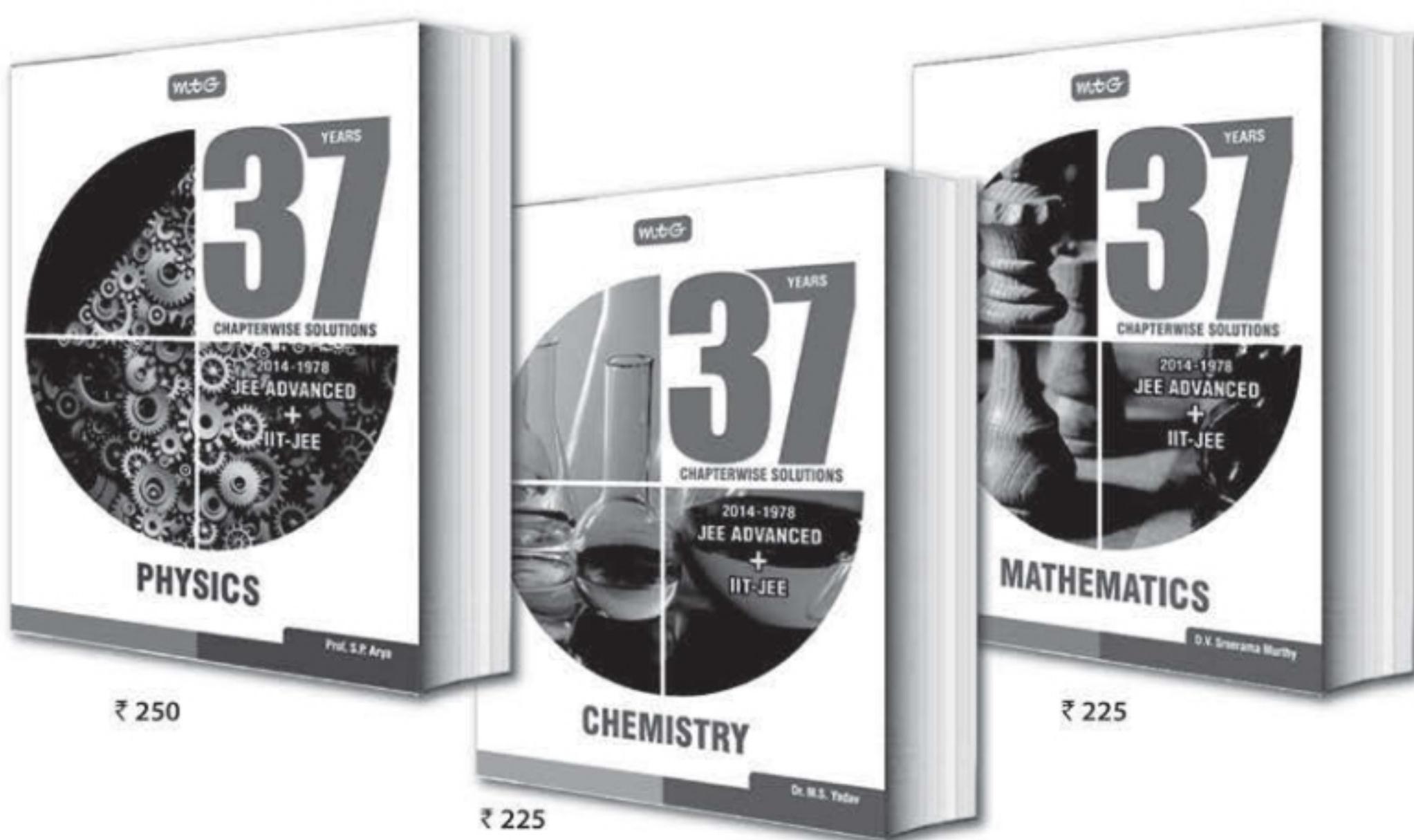
39. Assertion : Simple distillation is used to separate a mixture of chloroform (boiling point = 334 K) and aniline (boiling point = 457 K).

Reason : Organic liquids with sufficient difference in their boiling points can be separated by simple distillation.

40. Assertion : PbI₄ is a stronger reducing agent than SnI₄.

Reason : On going down the group 14 elements, higher oxidation state becomes more stable due to inert pair effect.

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SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

- 41.** Number of valence electrons in carbene is

42. Total number of π -bonds present in borazine is

43. On complete combustion, 0.22 g of an organic compound gave 0.176 g of carbon dioxide and 0.112 g of water. The percentage composition of hydrogen in the compound is

44. Amongst the following, the total number of groups showing $-I$ effect is
 $-\text{Cl}$, $-\text{NO}_2$, $-\text{CH}_3$, $-\text{CN}$, $-\text{COOR}$, $-\text{OC}_6\text{H}_5$

45. In silicones, one Si atom is attached to n number of oxygen atoms. Hence n is

46. Total number of alkyl groups having the molecular formula C_4H_9 are

47. Amongst the following, the maximum number of compounds which do not behave as Lewis acids are : SnCl_2 , H_3BO_3 , AlCl_3 , CF_4 , SiF_4 , SiCl_4 , CCl_4 , BF_3 , SnCl_4

48. Number of B—O—B bonds in borax is

49. In a compound C, H and N are present in 9 : 1 : 3.5 by weight. If molecular weight of the compound is 108, the number of H atoms present in the molecular formula will be

50. Number of mixed compounds of lead out of the following is
Lead monoxide, lead dioxide, red lead, basic lead carbonate, lead chloride and plumbic chloride.

SOLUTIONS

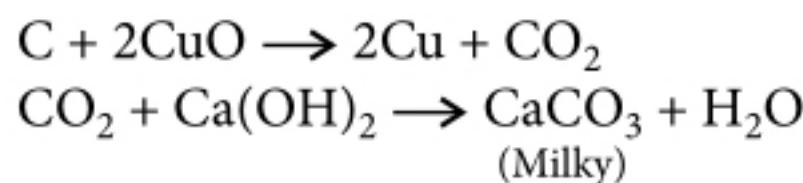
1. (a) : $\text{Sn} + 2\text{Cl}_2 \longrightarrow \text{SnCl}_4$

2. (a) 3. (b)

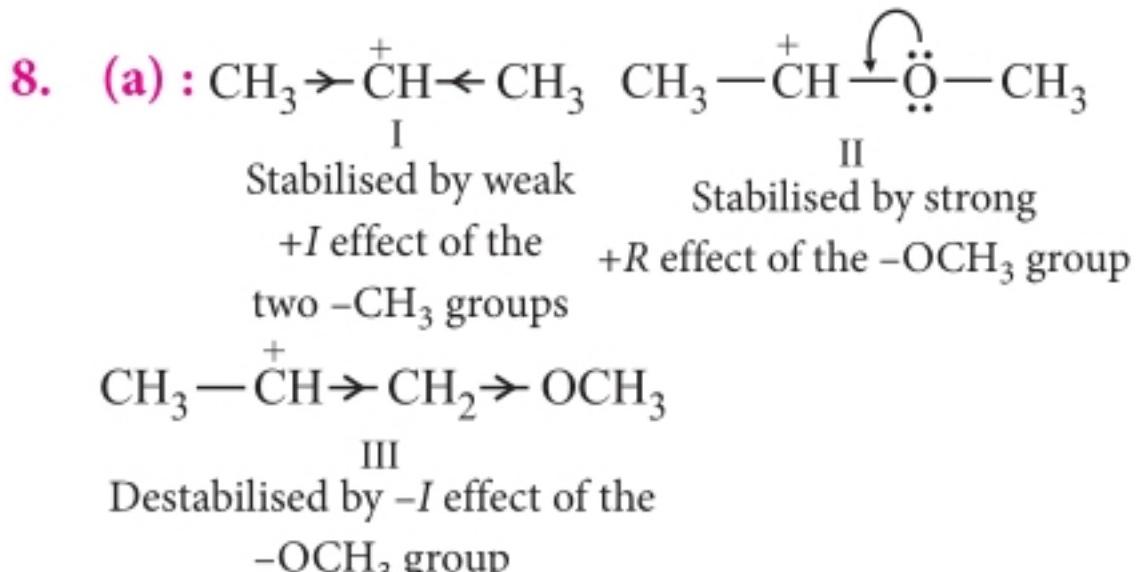
4. (a) : Acetoisonitrile is the incorrect name while all the remaining names are correct.

5. (b) : Stability of +3 oxidation state decreases from Al to Tl. B always shows +3 oxidation state in all of its compounds.

6. (b) : Compound when heated with CuO reduces CuO to Cu and oxidises C to CO_2 which turns lime water milky.



7. (d) : Orthoboric acid (H_3BO_3) contains triangular BO_3^{3-} units joined together through H-bonds forming a trigonal planar layer structure.



Thus, the stability of carbocations decreases in the order : $\text{II} \geq \text{I} \geq \text{III}$.

- 9. (d) :** Wood charcoal adsorbs large volume of gases from atmosphere.

10. (a) : On the basis of hyperconjugation, the order of stability of free radicals is as follows $3^\circ > 2^\circ > 1^\circ$. Benzyl free radicals are stabilised by resonance and hence are more stable than alkyl free radicals. More the number of phenyl groups attached to the carbon atom, more is the stability of free radical.

11. (a) : Boron has maximum covalency of four due to non-availability of *d*-orbitals. Boron does not form MF_6^{3-} ion but it forms complex fluoride of type BF_4^- .

- 12. (a) :** In (a), due to similar charges (two positive charges) on adjacent atoms, the structure is expected to be least stable.

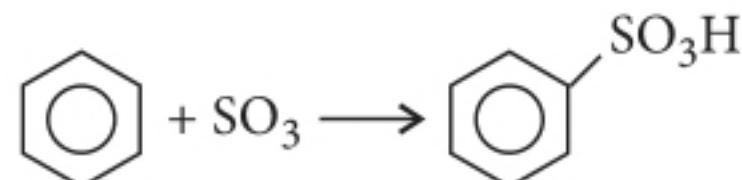
- 13. (b) :** CO is a Lewis base as it acts as a ligand in complexes.



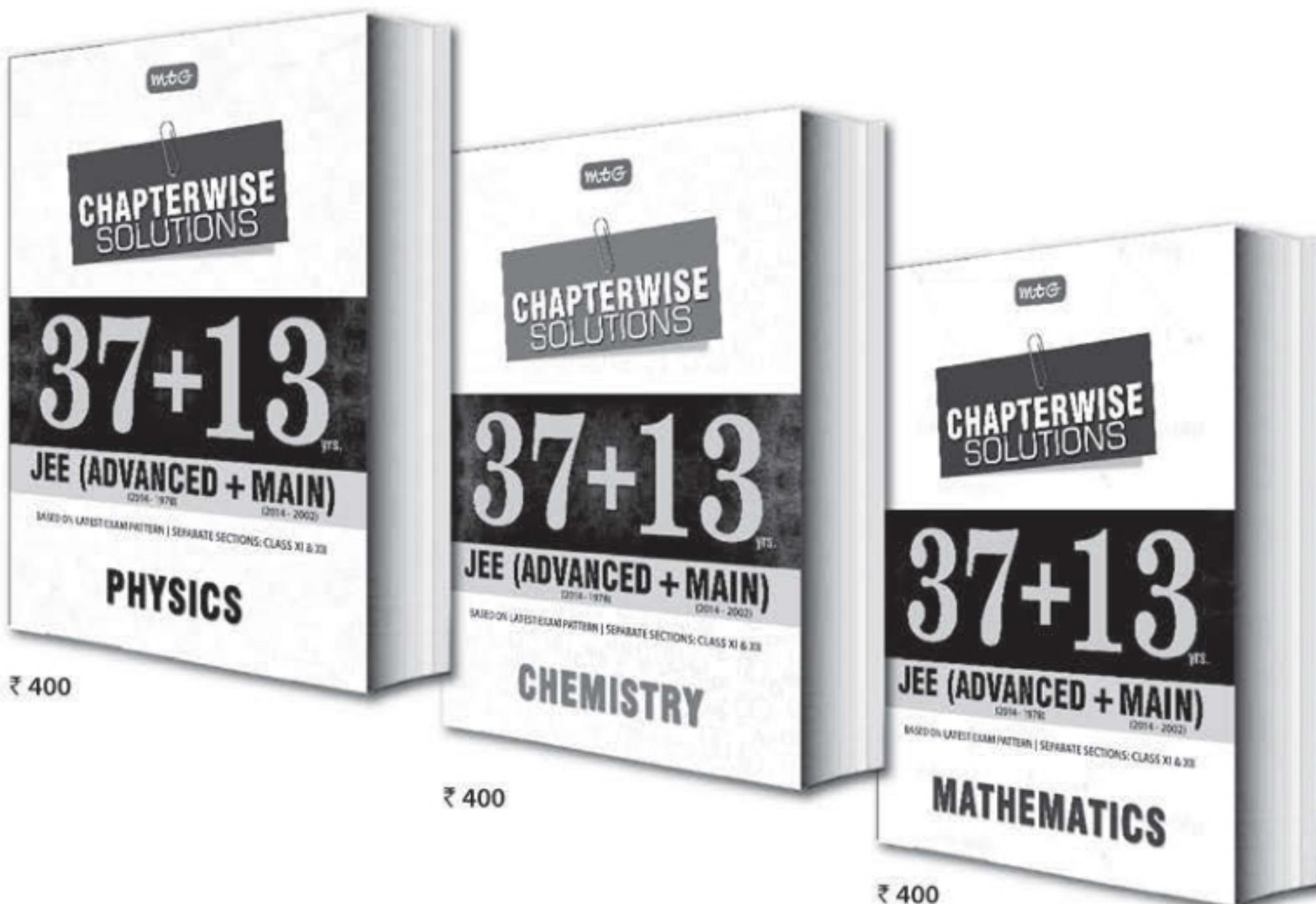
- 14. (b):** Homologues have different molecular formula, thus cannot be isomers.

- 15. (d):** CCl_4 under the name pyrene is incombustible and is used as a fire extinguisher.

- 16. (d) :** $2\text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_3 + \text{HSO}_4^- + \text{H}_3\text{O}^+$

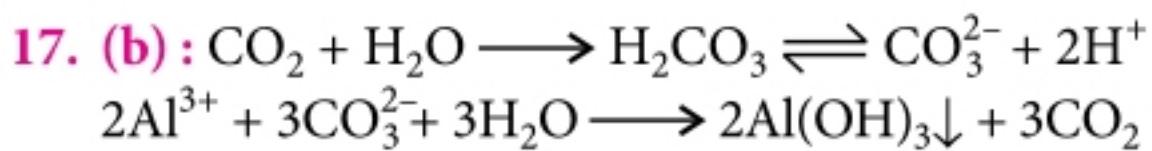


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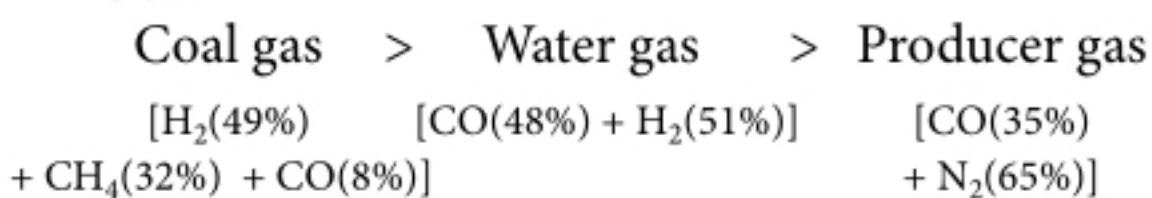
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18. (c) : The given reaction results in the formation of racemic mixture due to the absence of any suitable optically active reagent.

19. (a) : Calorific value follows the order :



20. (c) : Molecular formula of methyl vinyl ether (CH₃O—CH=CH₂ = C₃H₆O) is the same as that of propanal (CH₃CH₂CHO = C₃H₆O).

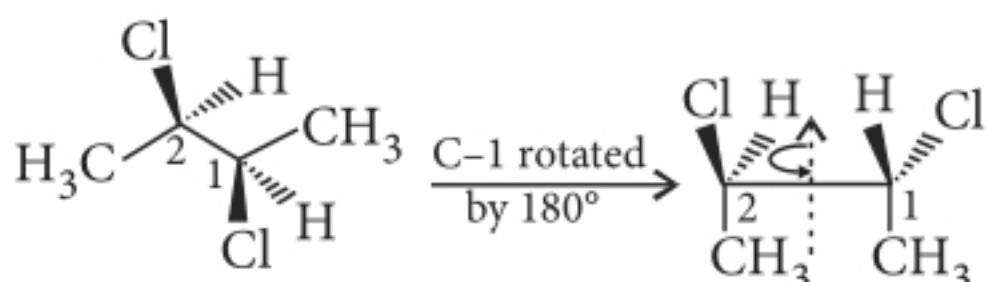
21. (b, c) : Fullerenes are cage-like molecules and graphite is the thermodynamically most stable allotrope of carbon. It is slippery and soft and hence, used as a dry lubricant in machines.

22. (b)

23. (a, b, c, d) : +1 oxidation state becomes stable along Ga⁺ < In⁺ < Tl⁺ while stability of +3 oxidation state is in the order Ga³⁺ > In³⁺ > Tl³⁺ due to inert pair effect.

Because of the same reason, tendency to show +2 oxidation state increases down the group 14 elements while stability of +4 oxidation state decreases.

24. (a, d) : The compound is optically active as it possesses two chiral centres.



The compound possesses axis of symmetry perpendicular to the C – C bond.

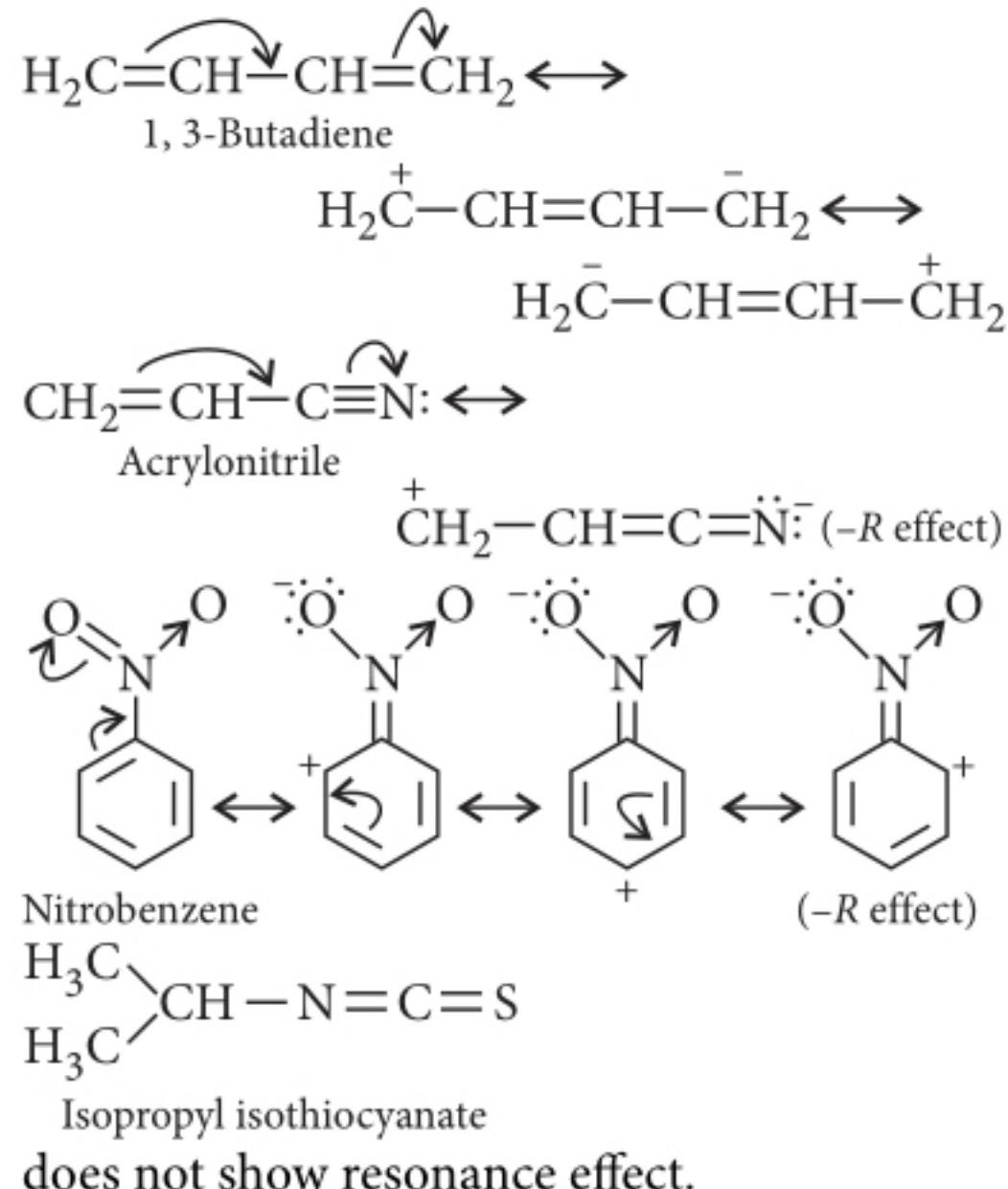
25. (c) : Borazine has a structure like benzene and is ionic in nature.

26. (c) : PbBr₄ does not exist because of highly oxidising power of Pb⁴⁺ ions and moderate reducing power of Br⁻ ions.

27. (c) : SiCl₄ is easily hydrolysed because Si can extend its coordination number beyond four due to the presence of vacant *d*-orbitals but carbon cannot do so in CCl₄ and hence is not hydrolysed.

28. (d) : CCl₄ is not acidic, all other compounds give acidic solutions on hydrolysis.

29. (d) : Resonance effect involves delocalisation of π -electrons of two or more conjugated double bonds or non-bonding electrons and π -electrons of a double bond.



Isopropyl isothiocyanate does not show resonance effect.

30. (a) : $-\text{N}(\text{CH}_3)_2$ shows +M effect while $>\text{C}=\text{O}$ and $-\text{CN}$ show -M effect.

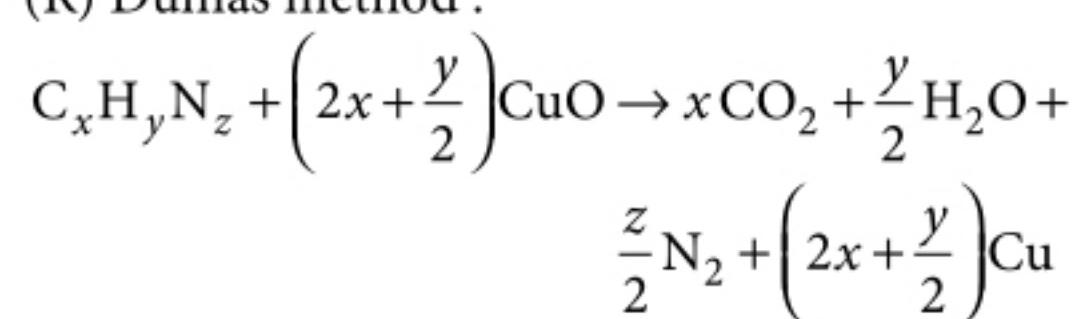
31. (d) : Stability of carboxylate ion depends on two factors : Electronegativity of the halogen atom and number of halogen atoms attached. More the electronegativity of the halogen atom and more the number of halogen atoms more will be the dispersal of negative charge.

32. (c)

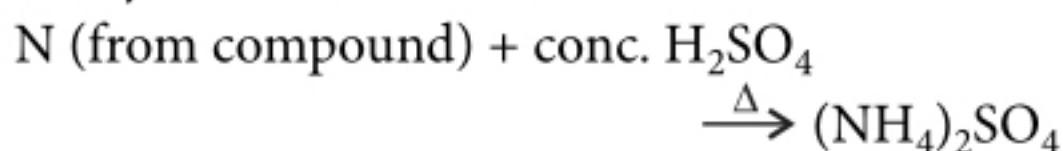
33. (b) : (P) $\text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3 \rightarrow$
 Ammonium molybdate

(Q) $\text{NaSCN} + \text{FeCl}_3 \rightarrow [\text{Fe}(\text{SCN})]\text{Cl}_2 + \text{NaCl}$
 Blood red

(R) Dumas method :



(S) Kjeldahl's method :



34. (a) : (P) Inductive effect is a permanent effect.
(Q) Resonance is the delocalisation of π electrons.
(R) No bond resonance or hyperconjugation is delocalisation of sigma electrons with π -bond.
(S) Electromeric effect is very strong effect.

35. (b) : Silicones are organosilicon polymers which have $-\text{R}_2\text{SiO}-$ as repeating unit. These are water repellent in nature because of the presence of cross-linking in their structure in the presence of moisture.

36. (c) : Steam distillation is based on volatility not on solubility.

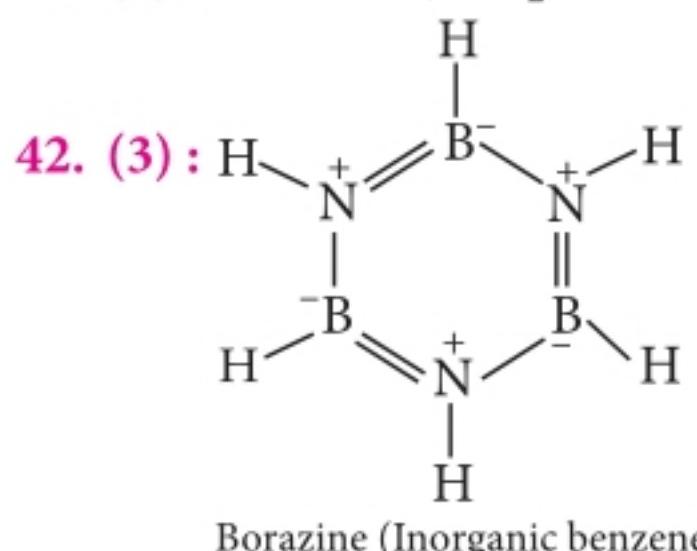
37. (a)

38. (c) : Orthoboric acid H_3BO_3 is soluble in water and behaves as a weak monobasic acid. It does not donate protons hence, it is not a protic acid. It is a Lewis acid as it accepts a lone pair of electrons.
 $\text{H}_3\text{BO}_3 + 2\text{H}_2\text{O} \longrightarrow [\text{B}(\text{OH})_4]^- + \text{H}_3\text{O}^+$

39. (a) : Simple distillation is used to separate volatile liquids those are stable at their boiling points and which contain non-volatile impurities having sufficient difference in their boiling points.

40. (d) : On going down the group 14, lower oxidation state becomes more stable than higher oxidation state due to inert pair effect. Pb^{4+} is less stable than Pb^{2+} , therefore, Pb^{4+} compounds are stronger oxidising agents than Sn^{4+} compounds.

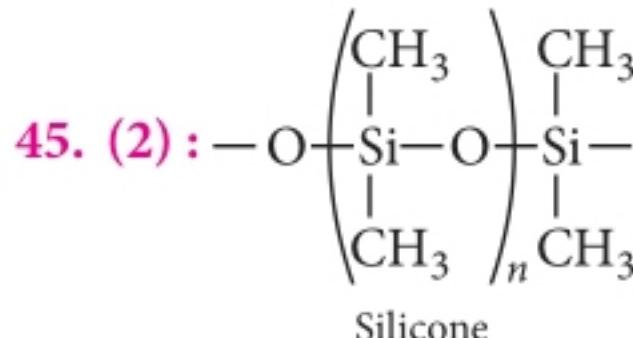
41. (6) : Carbene ($:\text{CH}_2$) has 6 valence electrons.



43. (6) : Percentage of hydrogen

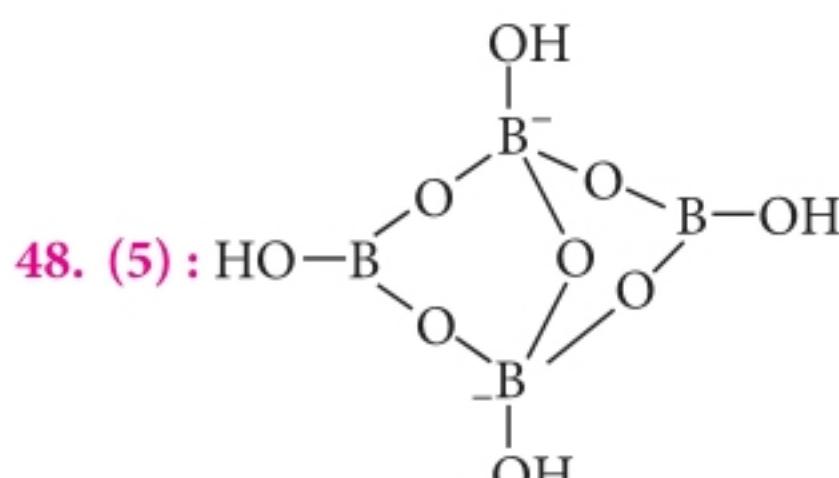
$$= \frac{2 \times \text{wt. of water}}{18 \times \text{wt. of organic compound}} \times 100 \\ = \frac{2 \times 0.112 \times 100}{18 \times 0.22} = 5.65\% \approx 6\%$$

44. (5) : $-\text{CH}_3$ is an electron donating group, therefore, shows $+I$ effect.



46. (4) : Four, i.e., *n*-butyl, isobutyl, *sec*-butyl and *tert*-butyl.

47. (3) : $\text{CF}_4, \text{SiCl}_4, \text{CCl}_4$.



49. (8) : C H N

$$\begin{array}{r} 9 \\ 9 \\ \hline 12 \end{array} : \begin{array}{r} 1 \\ 1 \\ \hline 1 \end{array} : \begin{array}{r} 3.5 \\ 3.5 \\ \hline 14 \end{array} \\ \begin{array}{r} 3 \\ 4 \\ \hline 1 \end{array} : \begin{array}{r} 1 \\ 1 \\ \hline 4 \end{array} \\ 3 : 4 : 1 \end{math>$$

Empirical formula = $\text{C}_3\text{H}_4\text{N}$

$(\text{C}_3\text{H}_4\text{N})_n = 108$

$(12 \times 3 + 1 \times 4 + 14)_n = 108$

$54n = 108 \Rightarrow n = 108/54 = 2$

Molecular formula = $\text{C}_6\text{H}_8\text{N}_2$

50. (2) : Lead monoxide (PbO) = single

Lead dioxide or Lead peroxide (PbO_2) = single

Red Lead or Trilead tetroxide

$(\text{Pb}_3\text{O}_4 = \text{PbO}_2 \cdot 2\text{PbO})$ = mixed

Basic lead carbonate (white lead)

$(2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2)$ = mixed

Lead chloride (PbCl_2) = single

Plumbic chloride (Lead tetrachloride) (PbCl_4)
= single





CONCEPT BOOSTER

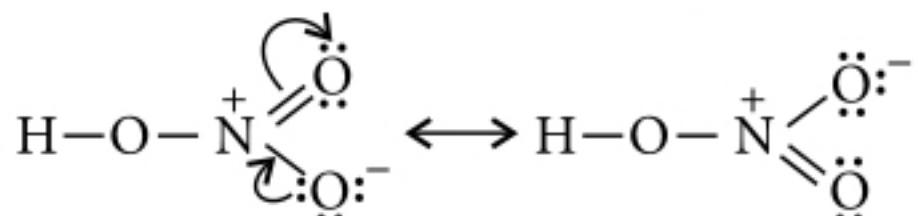
Dear students!! This is the second issue of the series of Inorganic Chemistry. In the last article I have shown the style to tackle the structural problem whereas in this issue you will get a snapshot of the process how to remember a chemical reaction in a smarter way. Main focus has been given on Nitric acid. I hope you will like it.

*Arunava Sarkar

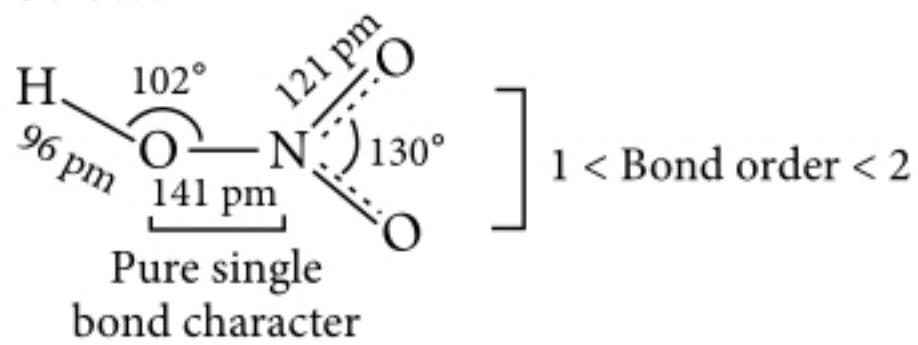
NITRIC ACID (HNO_3)

There are three oxoacids of nitrogen normally known. They are nitrous acid (HNO_2), nitric acid (HNO_3) and hyponitrous acid ($\text{H}_2\text{N}_2\text{O}_2$).

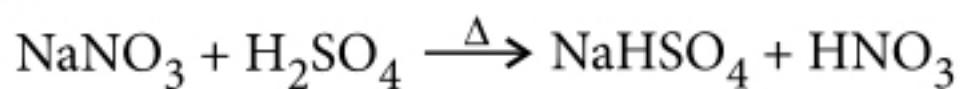
- The structure of HNO_3 can be given as below:



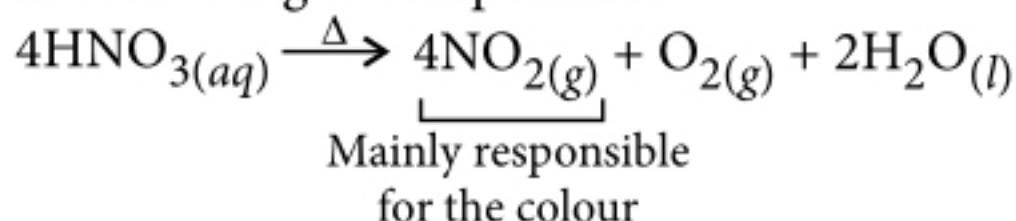
The planar resonance hybrid structure looks as below:



- In laboratory, reaction between potassium nitrate or sodium nitrate with conc. H_2SO_4 gives nitric acid.

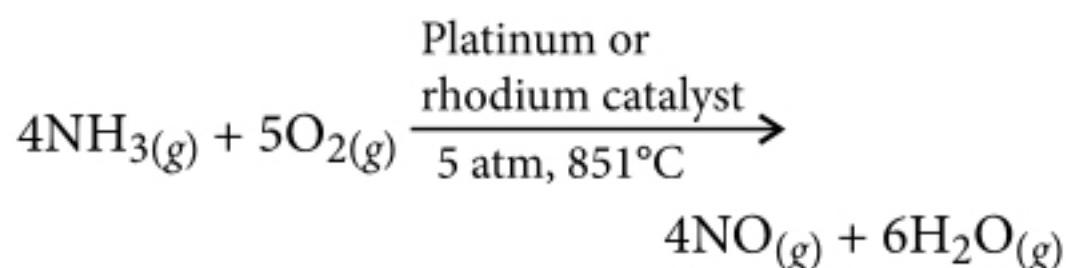


- Pure nitric acid is colourless but on exposure to light it turns brown or yellowish brown due to the following decomposition.

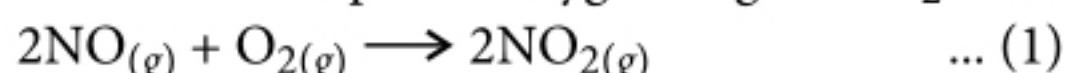


- Commercially, HNO_3 is prepared through Ostwald's process. Steps are as follows:

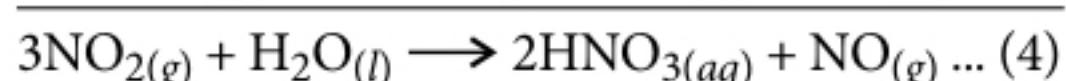
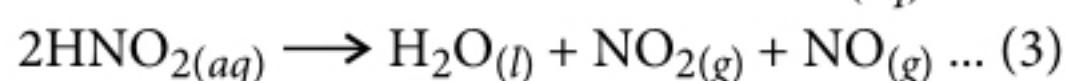
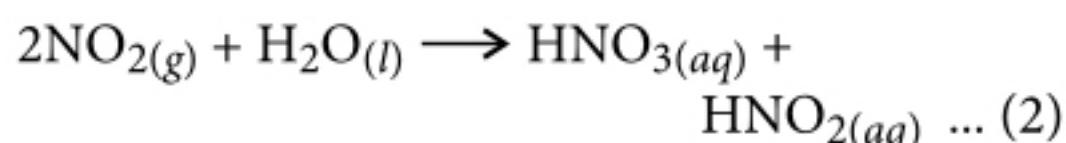
Step-I : At this step, catalytic oxidation of ammonia leads to the formation of nitric oxide.



Step-II : At this step, nitric oxide combines with the atmospheric oxygen to give NO_2 .



Step-III : Dissolution of NO_2 in water gives nitric acid (HNO_3). Stepwise reactions are as follows:



NO produced in (3) and (4) is recycled as in (1). HNO_3 is first 60% by mass. Distillation is thus important. Even today, a large amount of HNO_3 is produced through this process.

Ostwald was awarded Nobel Prize in the year 1909. Ostwald's process gives 68% by mass HNO_3 when it is concentrated by distillation. To get 98% conc. HNO_3 by mass it has to be dehydrated by conc. H_2SO_4 .

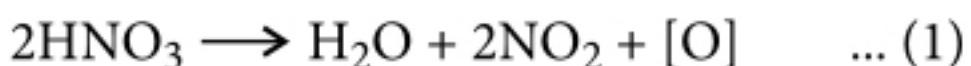
Important Reactions of HNO_3

1. Reaction with non-metals

HNO_3 reacts with a number of non-metals. It acts as an oxidising agent here. The non-metals get converted to their corresponding oxyacids.

(a) *Reaction with phosphorus :*

Step-1 : HNO_3 decomposes to give nascent oxygen.

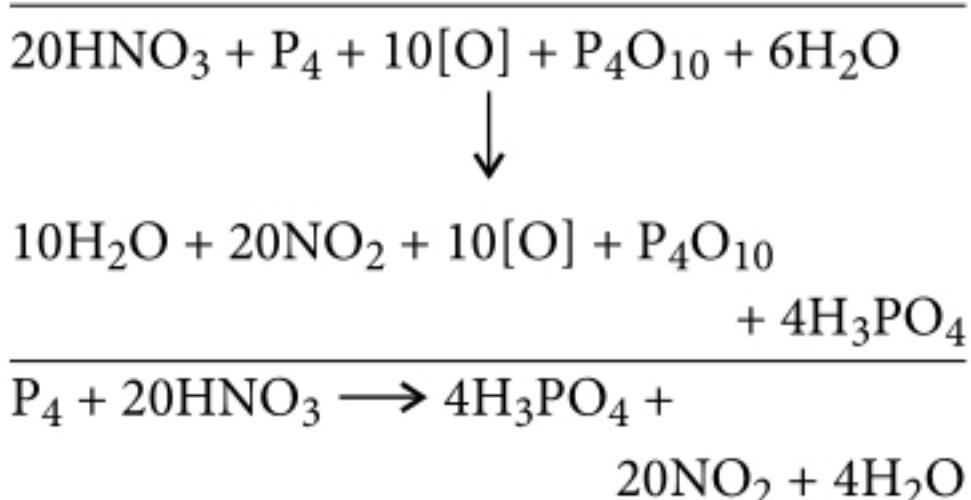


In this step always non-metal undergoes oxidation to give oxide.

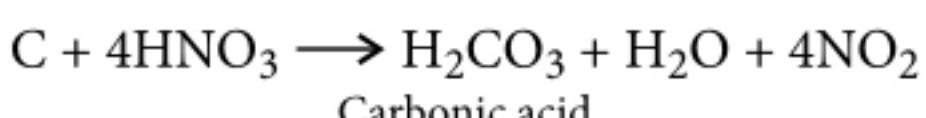
Step-3 : Oxide dissolves into water to give the oxyacid.



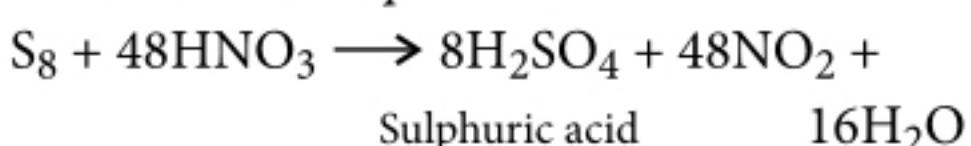
$$[(1) \times 10] + (2) + (3) \text{ gives}$$



(b) *Reaction with carbon :*



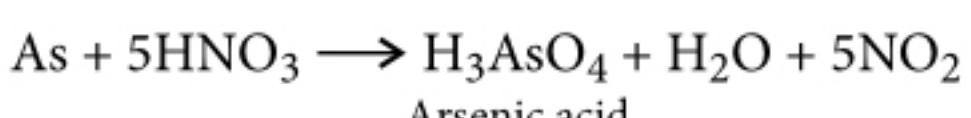
(c) *Reaction with sulphur :*



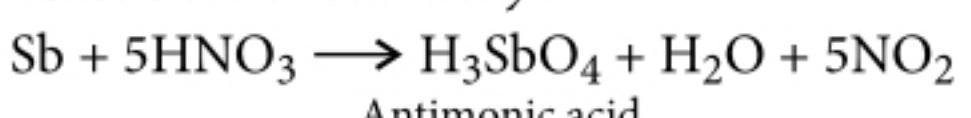
(d) *Reaction with iodine :*



(e) *Reaction with arsenic :*



(f) *Reaction with antimony :*

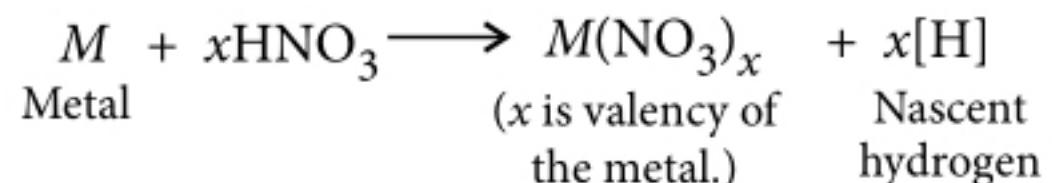


2. Reaction with metals

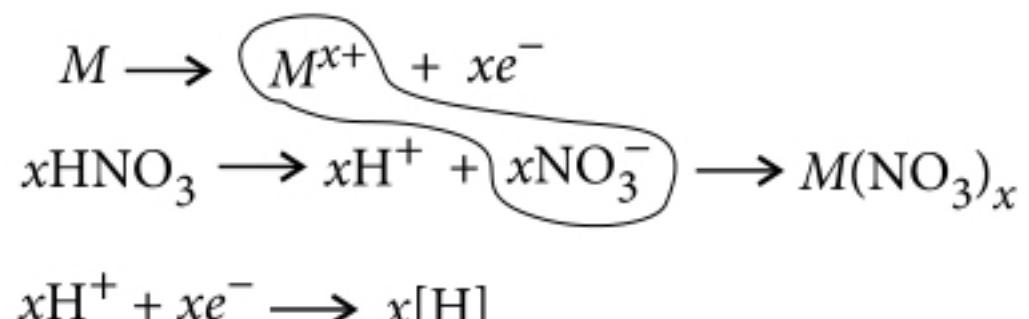
HNO_3 is very good at reaction with metals with the exceptions of few, not so reactive metals like gold, platinum which are into the class of noble metals. Style of reaction depends on the nature of HNO_3 solution like whether cold or hot and whether dilute or concentrated. Moreover, reactivity of metals also greatly influence the overall reaction. Based on this different categories of reactions are :

I. Reaction with active metals which in the electrochemical series are higher in position than hydrogen.

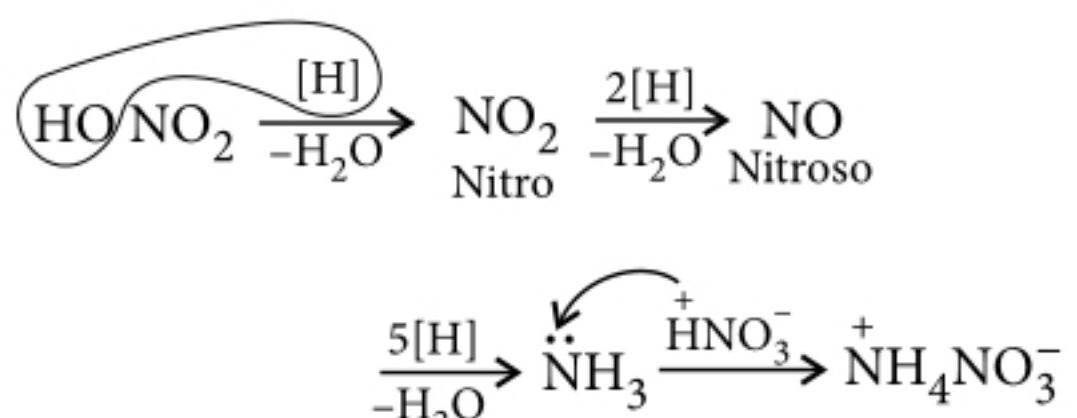
Formation of nitrate is a must here. Metals are oxidised and HNO_3 is reduced. Strategy is as follow:



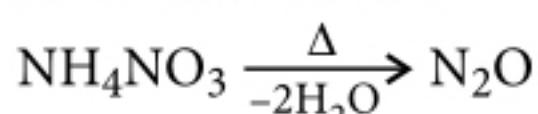
Mechanism is strictly electron transfer.



This nascent hydrogen reduces HNO_3 in the similar manner as in case of organic nitro compounds.



Now, applying heat on NH_4NO_3 , nitrous oxide is a product but it is only possible by applying heat otherwise not.

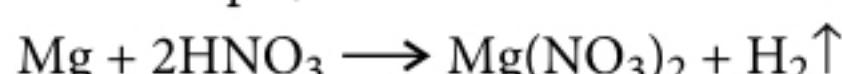


(a) Very dilute HNO_3 :

Two cases happen here mainly:

- (i) Less amount of HNO_3 does not allow nascent hydrogen for any further reduction.
- (ii) Dilute HNO_3 undergoes more dissociation to give more amount of nascent hydrogens which on combination give H_2 gas.

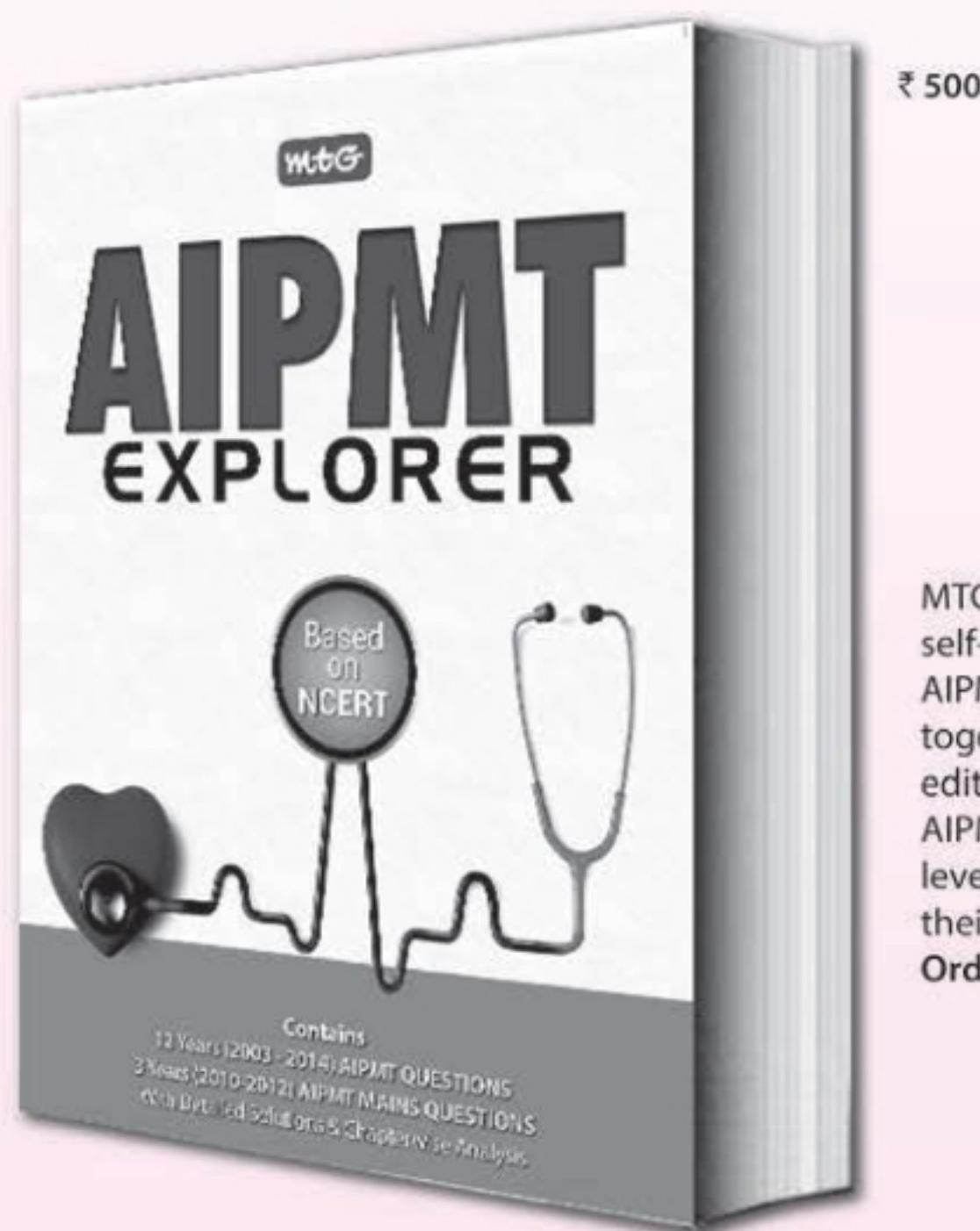
For example,



(b) Cold, moderately dilute (not very dilute) HNO_3 :

Stop the reaction at ammonium nitrate stage.

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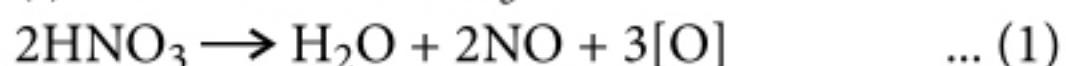
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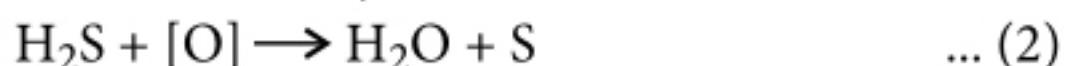
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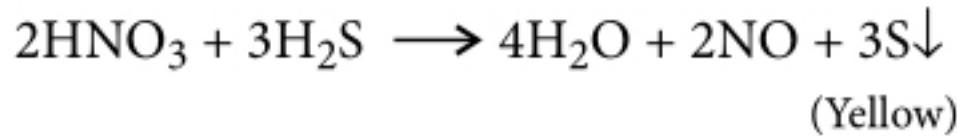
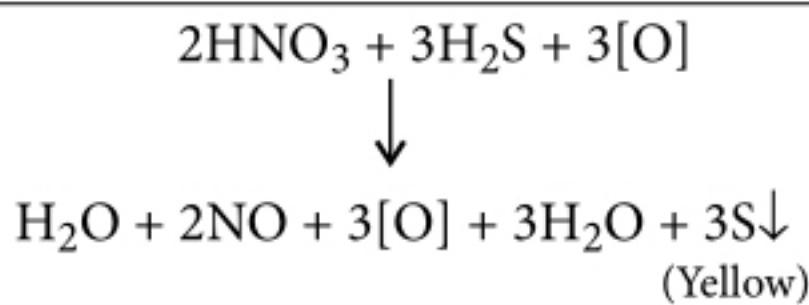
(i) With dilute HNO_3 :



(NO_2 is produced at first which is further reduced to NO .)



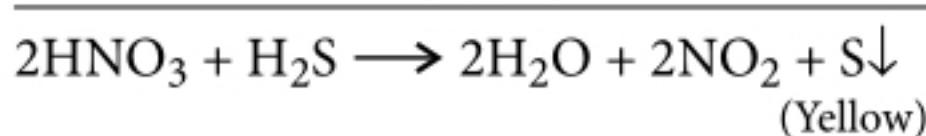
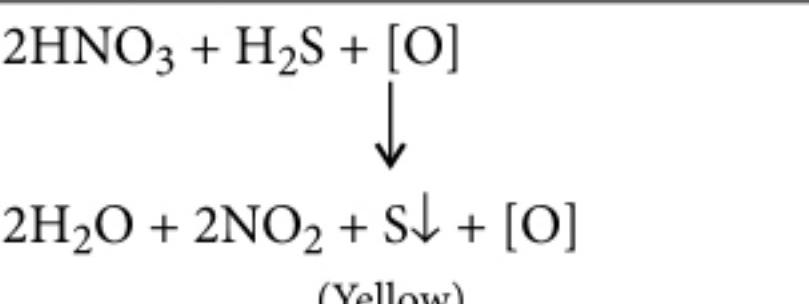
$(1) \times 1] + [(2) \times 3]$ gives



(ii) With conc. HNO_3 :



$(1) + (2)$ gives

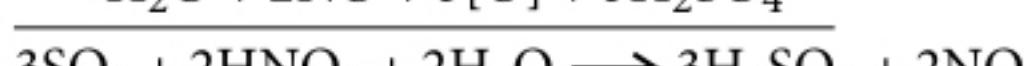
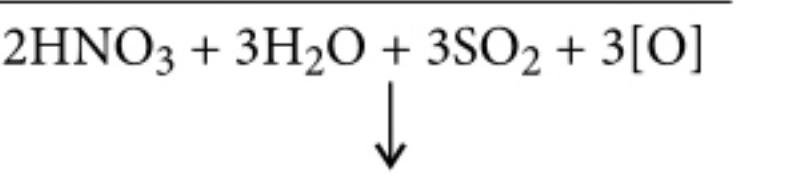


(b) With SO_2 : Here an extra strategy has to be added. As SO_2 is a gas, hence, it will undergo dissolution in H_2O and thus H_2SO_4 will be an expected product.

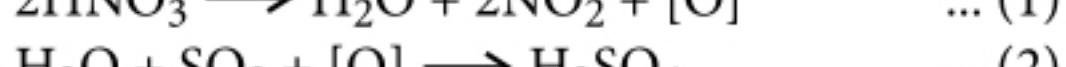
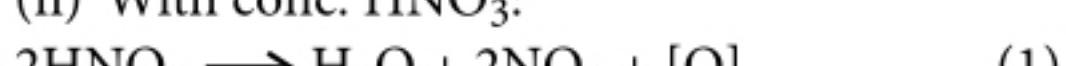
(i) With dilute HNO_3 :



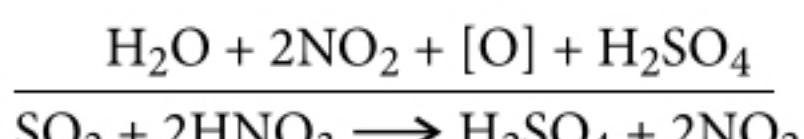
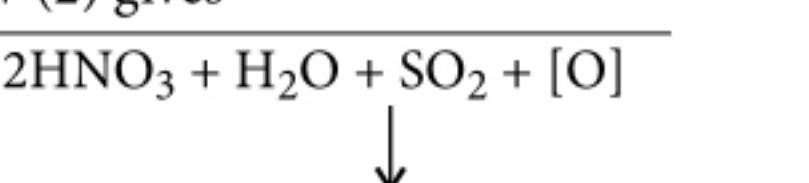
$(1) + [(2) \times 3]$ gives



(ii) With conc. HNO_3 :



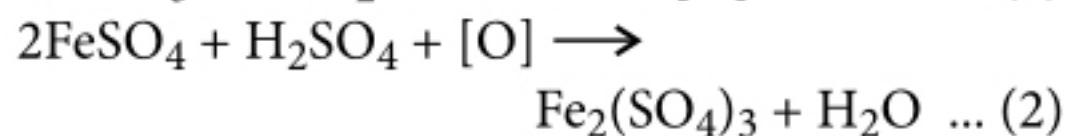
$(1) + (2)$ gives



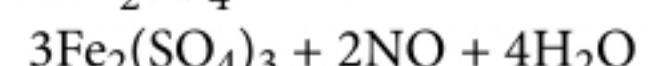
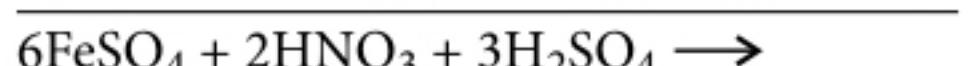
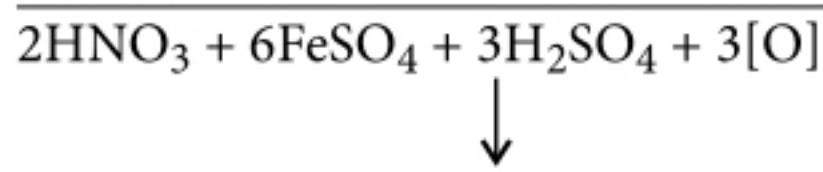
(c) With FeSO_4 :

FeSO_4^{2+} is the point of discussion because Fe^{2+} can be oxidised to Fe^{3+} . i.e. FeSO_4 can be converted to $\text{Fe}_2(\text{SO}_4)_3$. Approach will be same if any other metal of same type is taken. Just remember one trick that to convert FeSO_4 into $\text{Fe}_2(\text{SO}_4)_3$, H_2SO_4 is needed along with the nascent oxygen.

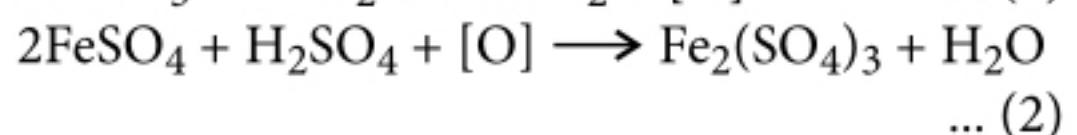
(i) With dilute HNO_3 :



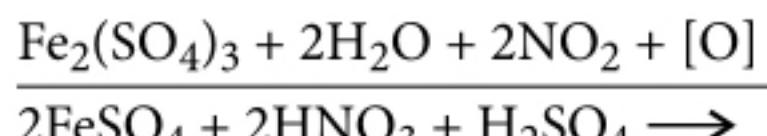
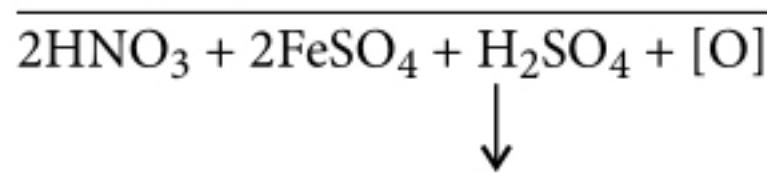
$(1) + [(2) \times 3]$ gives



(ii) With conc. HNO_3 :



$(1) + (2)$ gives



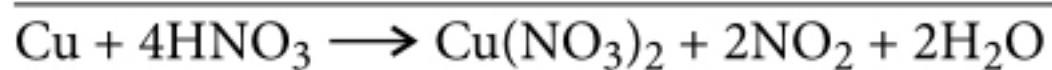
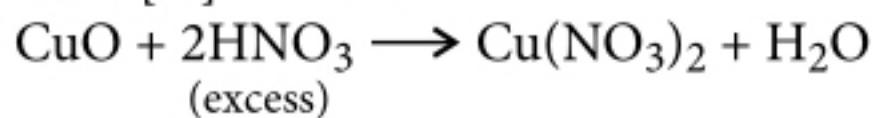
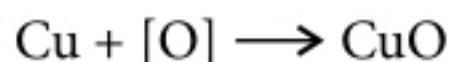
III. Reaction with metals which are at lower position with respect to hydrogen (except noble metals).

An obvious trick is H_2 will not be liberated here. Here, metal is oxidised at first to the corresponding metal oxide which on further reaction with HNO_3 gives metal nitrate. HNO_3 in this process can be converted either to NO_2 or to NO . This is found that when concentrated HNO_3 is used, NO_2 is produced and with dilute HNO_3 , NO is produced.

Case (a) : Reaction of Cu, Hg, Ag with conc. HNO_3 :



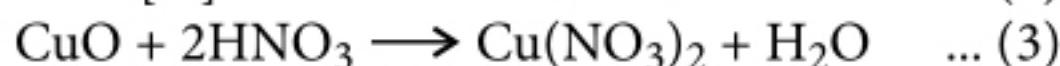
Responsible for
oxidation of metal



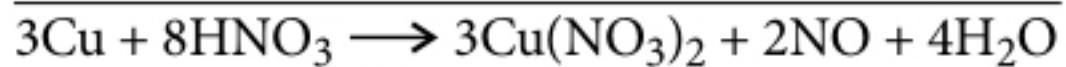
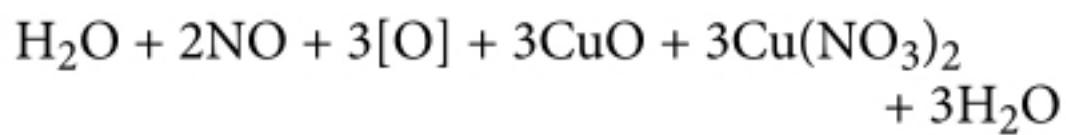
Hg and Ag will give similar reactions.

Case (b) : Reaction of Cu, Hg, Ag with dilute HNO_3 :

Here NO will be a product of the decomposition of HNO_3 . For example,



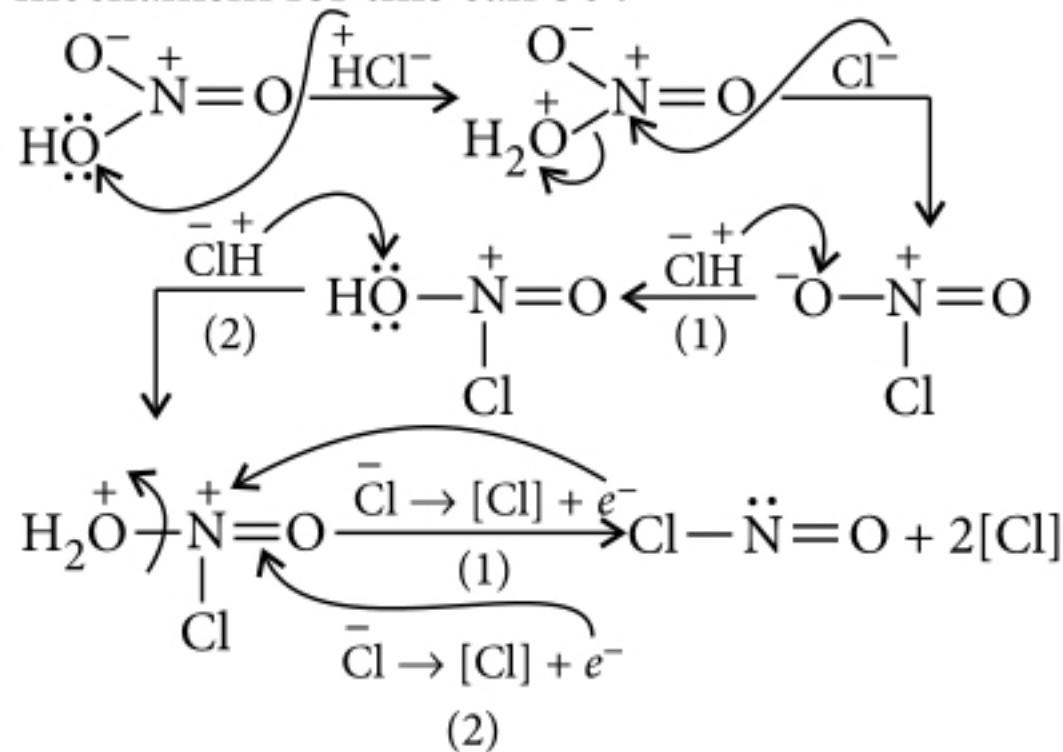
(1) + [(2) \times 3] + [(3) \times 3] gives



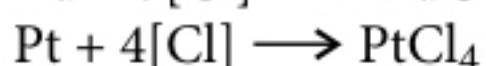
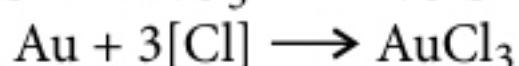
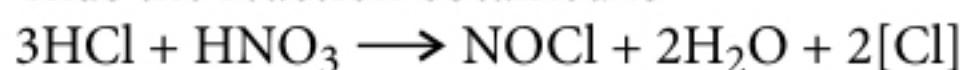
Ag and Hg under similar condition give the similar reaction.

- Now, here comes the reaction of noble metals with HNO_3 .

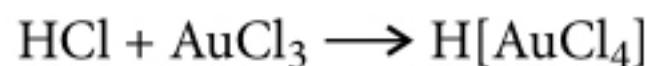
Basically, as Au and Pt are very non-reactive therefore, they do not react even with conc. HNO_3 . Rather they react with 3 : 1 ratio of mixture of conc. HCl and conc. HNO_3 which is known as **aqua regia**. Here, at first reaction between HCl and HNO_3 gives NOCl (nitrosyl chloride) and nascent chlorine. A probable mechanism for this can be :



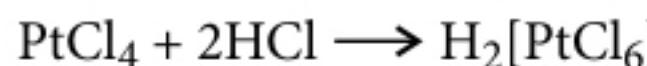
Thus the reaction obtained is



These chlorides dissolve in excess of HCl giving soluble complexes like $\text{H}[\text{AuCl}_4]$ or $\text{H}_2[\text{PtCl}_6]$.



Aurochloric acid



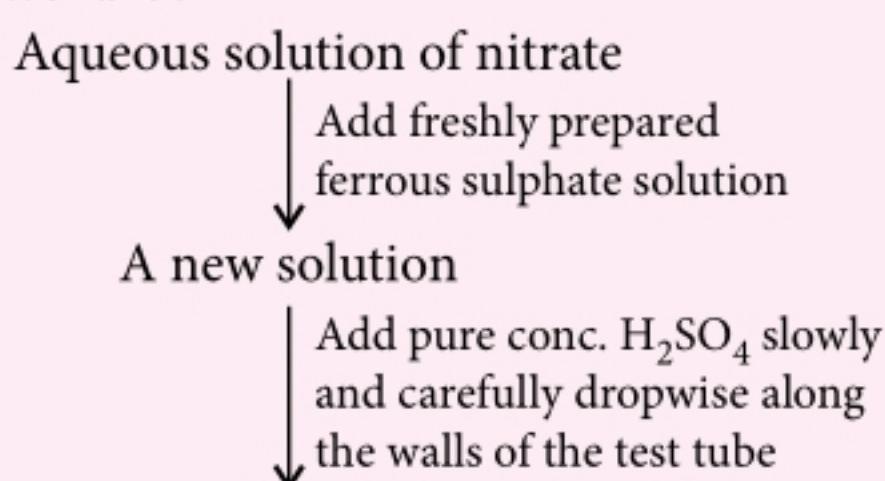
Chloroplatinic acid

Add to your Knowledge

Ring Test

It is a test (in fact confirmatory test) for nitrate ions.

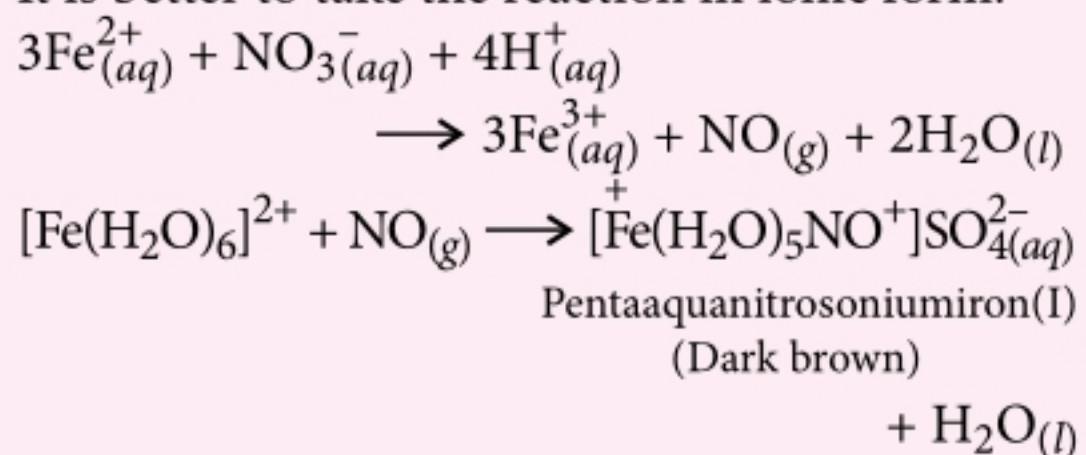
Flowchart :



A dark brown ring (hence the name ring test) is obtained at the junction of the two layers.

Reaction is as follows:

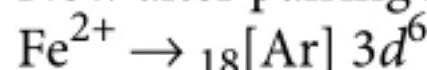
It is better to take the reaction in ionic form.



$3d$	$4s$	$4p$
1↑ 1 1 1 1	□	□ □ □

NO imparts the strong field to pair up the electrons along with water molecules which are working as the ligands.

Now after pairing it looks as



$3d$	$4s$	$4p$
1↑ 1↑ 1↑ □	↑	↑ ↑ ↑
$\text{H}_2\ddot{\text{O}}$	$\text{H}_2\ddot{\text{O}}$	$\text{H}_2\ddot{\text{O}}$ $\text{H}_2\ddot{\text{O}}$ NO

Surprised!! ←

Due to the presence of single electron dot, NO is in much more need of linking up than that of H_2O . So, remember that due to single electron donation, here Fe is not in the Fe^{2+} form rather than in Fe^{1+} form and NO is also present as NO^+ .

... To be continued on the next issue.





ADVANCED CHEMISTRY BLOC

(ENTROPY AND ENTROPY CHANGE)

Mukul C. Ray, Odisha

Entropy

In Carnot cycle (perfect gas, reversible process), the following cyclic integral is zero.

$$\int \frac{dq_{rev.}}{T} = 0, \text{ Carnot cycle, Perfect gas}$$

Since the above integral is zero around any reversible

cycle, it follows that the value of the integral $\int_1^2 \frac{dq_{rev.}}{T}$

is independent of the path between the states 1 and 2 and depends only on the initial and final states.

Hence $\frac{dq_{rev.}}{T}$ is the differential of a state function.

This state function is called as the entropy S .

$$dS \approx \frac{dq_{rev.}}{T}, \text{ Closed system, Reversible process}$$

Since internal energy U is a state function, the differential dU is a state function and the value of the integral of dU between two states depends only on the states and not on the path. It is done exactly in a reverse way that since the value of the integral

$\int_1^2 \frac{dq_{rev.}}{T}$ depends only on the states therefore,

the differential $\frac{dq_{rev.}}{T}$ is the differential of a state

function and that state function is the entropy.

The entropy change in going from the state 1 to state 2 equals the integral:

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dq_{rev.}}{T},$$

Closed system, Reversible process

The value of ΔS is same for any process that connects the states 1 and 2 as it is a state function. But it is only for a reversible process the integral $\int \frac{dq_{rev.}}{T}$ gives the entropy change.

Entropy Change

Ways to calculate ΔS for some processes are given. Here ΔS means ΔS_{sys} .

○ Cyclic process:

Since entropy is a state function, $\Delta S = 0$ for every cyclic process.

○ Reversible adiabatic process:

For adiabatic process, $dq_{rev.} = 0$ therefore, $\Delta S = 0$, for a reversible adiabatic process.

○ Reversible phase change at constant temperature and pressure:

At constant T

$$\Delta S = \int_1^2 \frac{dq_{rev.}}{T} = \frac{1}{T} \int_1^2 dq_{rev.} = \frac{q_{rev.}}{T}$$

$1/T$ is taken outside as T is a constant and $q_{rev.}$ is the latent heat of transition. Since P is constant and $q_{rev.} = q_p = \Delta H$, therefore,

$$\Delta S = \frac{\Delta H}{T}, \text{ for a reversible phase change at constant } T \text{ and } P.$$

○ Reversible isothermal process:

Here T is a constant, and

$$\Delta S = \int_1^2 \frac{dq_{rev.}}{T} = \frac{1}{T} \int_1^2 dq_{rev.} = \frac{q_{rev.}}{T},$$

for a reversible isothermal process.

O Heating at constant pressure with no phase change:

Consider the heating that is done reversibly at constant pressure provided no phase change occurs, $dq_{\text{rev}} = dq_p = C_p dT$. Thus,

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT, \text{ at constant } P, \text{ no phase change.}$$

If C_p is essentially a constant over the temperature range, then

$$\Delta S = C_p \ln \frac{T_2}{T_1}$$

O Reversible state change of a perfect gas:

From first law,

$$dq_{\text{rev}} = dU - dw_{\text{rev}} = C_v dT + PdV \\ = C_v dT + nRT \frac{dV}{V}$$

$$\text{or } dS = \frac{dq_{\text{rev}}}{T} = \frac{C_v dT}{T} + nR \frac{dV}{V},$$

$$\text{or } \Delta S = \int_{T_1}^{T_2} \frac{C_v dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\text{or } \Delta S = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}, \text{ for a perfect gas.}$$

O Mixing of perfect gases:

For mixing of perfect gases,

$$\Delta S_{\text{mix}} = -R \sum n_i \ln x_i \text{ for a perfect gas, at constant } T \text{ and } P.$$

where n_i and x_i represent the number of moles and the mole fraction respectively, of each constituent of the mixture.

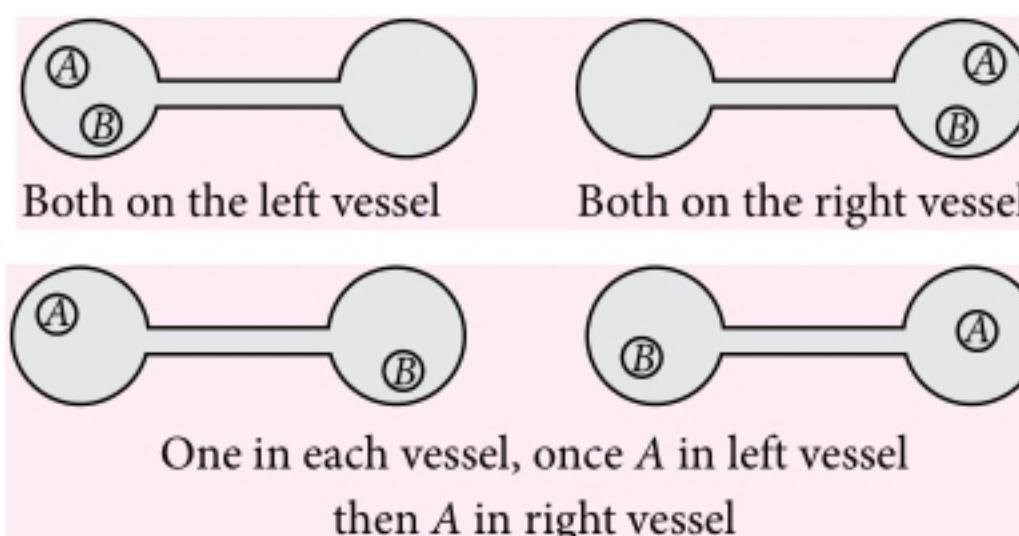
What is Entropy?

Although there is no simple definition that is completely accurate, entropy can be viewed as a measure of molecular randomness or disorder. The natural progression of things is from ordered state to disordered state that is from lower entropy to higher entropy.

Suppose there is a deck of playing cards ordered in some particular way. These cards are thrown into the air and picked up at random. Looking at the new sequence of cards, it would be very surprising

to find that it matched the original order. Such an event would be possible but very improbable. There are billions of ways for the deck of cards to be disordered, but only one way to be ordered. Thus the chances of picking the cards out of order are much greater than the chance of picking them in order. If the ordered state is taken as one macrostate and disordered state as another macrostate then one thing is clear there is only one way of getting them ordered or the ordered macrostate has only one microstate and the disordered macrostate has a billions of microstates means a billions of ways to get the disordered state.

For any macrostate, the number of microstates is directly proportional to entropy. The process has a tendency to move towards that state which has higher probability of existence or higher entropy. Furthermore, entropy is a thermodynamic function that describes the number of arrangements that are available to a system existing in a given state. Consider two molecules named A and B to be distributed in between two vessels.



The probability that both will be on the left is thus 1/4, whereas the probability that they are equally distributed in two vessels is 2/4 or 1/2. This means the macrostate that has one molecule in each vessel is made up of two microstates whereas the macrostate in which both of them are on the left has just one microstate. So naturally, the molecules will have a tendency to remain equally distributed

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between the two vessels. That is why gases have a tendency to fulfill the container uniformly.

The process moves towards that state which has more probability of existence or made up of more microstates. The great Boltzmann gave the relation between the number of microstates and the absolute entropy.

$$S = k \ln w$$

where k is the Boltzmann constant and w is the microstates in a macrostate.

Positional and Energy Disorderness

Suppose there is a sample of gas in a closed container. Now there are few energy levels, which the molecules can access. On increasing the temperature or expanding the volume, more energy levels will be available to the gas sample. On increasing the volume, the total energy remains constant but more energy levels closer to each other would develop. This is called positional disorderness or probability. On increasing the temperature not only the total energy would increase but also there will be more levels too. This is called energy disorderness or probability. Ultimately everything is linked to energy and energy has a tendency to get spread out. So a gas expands into vacuum because the expanded state has the highest positional probability.

Entropy, Reversibility and Irreversibility

The total entropy change of the process is the sum of the entropy change of the system as well as surrounding.

$$\Delta S_{\text{sys.}} + \Delta S_{\text{surr.}} = 0$$

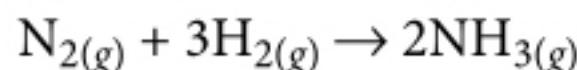
For a reversible process, although entropy of system and surrounding may change but:

$\Delta S_{\text{univ.}} = 0$, Reversible process

$\Delta S_{\text{univ.}} > 0$, Irreversible process

The processes are spontaneous when they result in increase in disorderliness. Nature always moves towards the most probable state available to it. This is said in terms of entropy. In any spontaneous process there is always an increase in entropy of the universe. This is the **second law of thermodynamics**. In contrast to first law, which says energy of the universe, is constant. Second law defines entropy and says it is not constant. Entropy can be created but not destroyed.

Consider synthesis of ammonia:



Four moles of gaseous substances are consumed and two moles are formed. This means entropy of the system is decreasing or in other words entropy change of the system is negative. This reaction is exothermic and energy is released. This released energy raises the entropy of the surrounding. Together entropy change of the system and surrounding makes $\Delta S_{\text{univ.}} > 0$ and the process a spontaneous one. On increasing temperature, $\Delta S_{\text{surr.}}$ decreases and beyond certain temperature that is around $450^\circ C$, the process is no more spontaneous. This signifies the importance of temperature in spontaneity. But if thermal decomposition of solid ammonium chloride to gaseous ammonia and HCl is considered the process is endothermic and more and more spontaneous as temperature increases. There are some simple examples as well; evaporation of water is spontaneous only above $100^\circ C$.



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UNIT-5

p-Block Elements (Group 15 to 18) | d- and f-Block Elements | Coordination Compounds | Environmental Chemistry

p-BLOCK ELEMENTS (GROUP 15 TO 18)

- Electronic configuration
- General Trends in Physical and Chemical Properties
- Allotropic forms
- Structure, Preparation, Properties and Uses of Some Important Compounds

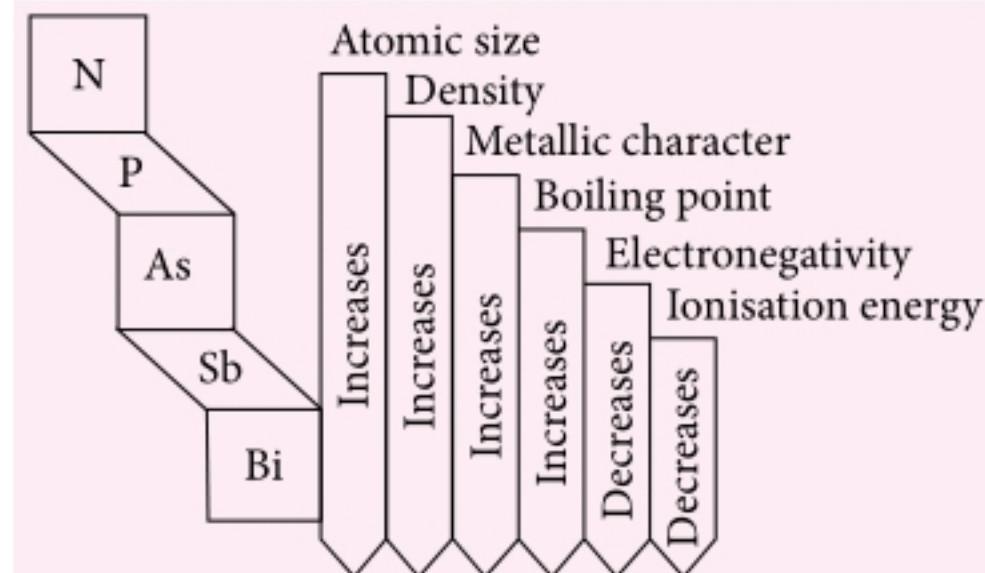
TIPS TO REMEMBER

- Elements in which the last electron enters any one of the three *p*-orbitals of their respective outermost shells are called *p-block elements*.

GROUP-15 ELEMENTS (NITROGEN FAMILY)

- General outer electronic configuration is ns^2np^3 , where $n = 2$ to 6.
□ They are collectively called as *pnictogens*.

Element	At. No.	Electronic configuration	Oxidation No.
Nitrogen (N)	7	[He] $2s^22p^3$	-1, -2, -3, 0, +1, +2, +3, +4, +5
Phosphorus (P)	15	[Ne] $3s^23p^3$	-3, +3, +5
Arsenic (As)	33	[Ar] $3d^{10}4s^24p^3$	-3, +3, +5
Antimony (Sb)	51	[Kr] $4d^{10}5s^25p^3$	-3, +3, +5
Bismuth (Bi)	83	[Xe] $4f^{14}5d^{10}6s^26p^3$	+3, +5



- $\underbrace{N, P}_{\text{Non-metals}}, \underbrace{As, Sb}_{\text{Metalloids}}, \underbrace{Bi}_{\text{Metal}}$
□ **Allotropy** : All the elements except Bi show allotropy.

Element	Allotropic Forms
Nitrogen	α -nitrogen, β -nitrogen
Phosphorus	white, red, scarlet, violet, α -black, β -black
Arsenic	grey, yellow, black
Antimony	metallic, yellow, explosive

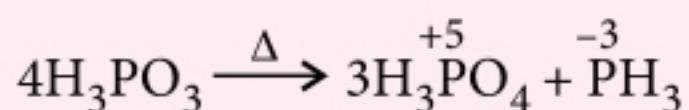
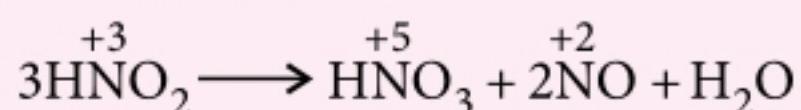
- **Catenation** : They exhibit the property of catenation to less extent than group 14 elements due to weak M—M bond.

Bond : C—C N—N P—P As—As

Bond energy : 347 159 213 147.4 (kJ/mol)

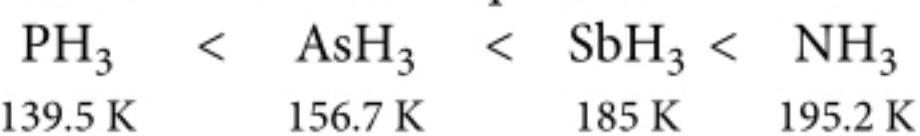
KEY POINT

- Melting point first increases from N to As and then decreases to Sb and Bi.
- 3 O.S. is exhibited by other elements also e.g., Ca_3P_2 , Na_3As , Zn_3Sb_2 .
- On moving down the group, the stability of +5 oxidation state decreases while that of +3 oxidation state increases due to ***inert pair effect***.
- Nitrogen shows disproportionation in acidic medium whereas phosphorus shows disproportionation in both acidic as well as basic medium.



Hydrides : Form $M\text{H}_3$ type hydrides.

- O Melting point :** Hydrides of group 15 elements follow the sequence :



- O Boiling point :**



The unusual order is probably due to the reason that the increase in the boiling points of SbH_3 and BiH_3 (because of higher van der Waals' forces of attraction) more than compensates the increase in boiling point of NH_3 (because of H-bonding).

Stability, Basic character, Bond angle,
Strength of $M-\text{H}$ bond decreases.

Bond angle : NH_3 (107.8°), PH_3 (93.6°), AsH_3 (91.8°), SbH_3 (91.3°), BiH_3 (90.0°)

Reducing character, Acidic character,
Poisonous character increases.

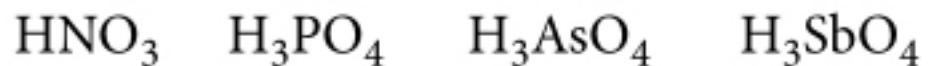
Oxides : All these elements form oxides of the type $X_2\text{O}_3$, $X_2\text{O}_4$ and $X_2\text{O}_5$.

N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3	↓ Acidic nature increases
N_2O_4	P_2O_4	As_2O_4	Sb_2O_4	Bi_2O_4	
N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	Bi_2O_5	

Acidic nature decreases →

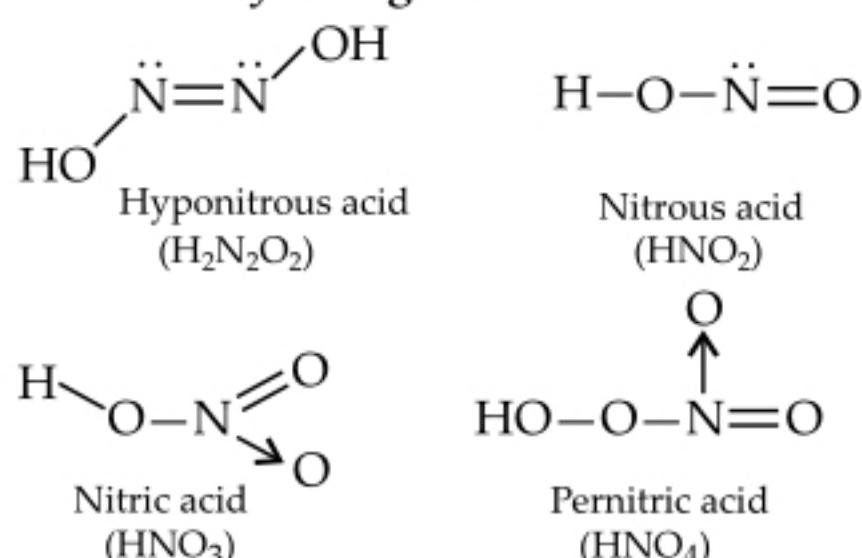
As the electronegativity increases, acidic character of the oxide also increases. Among the oxides of same element, higher the oxidation state, greater the acidic character.

□ Oxoacids : The strength and stability of oxoacids having the element in the same oxidation state decrease gradually with decrease in electronegativity of the central atom.



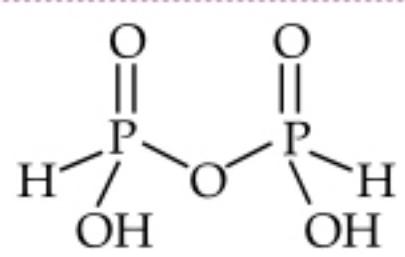
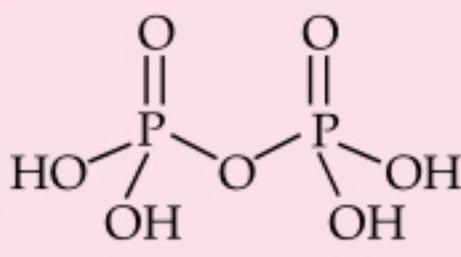
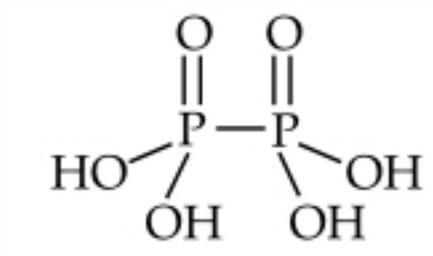
Stability decreases →

O Oxoacids of nitrogen :



O Oxoacids of phosphorus :

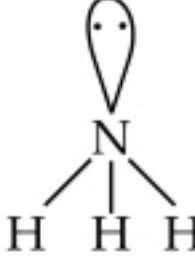
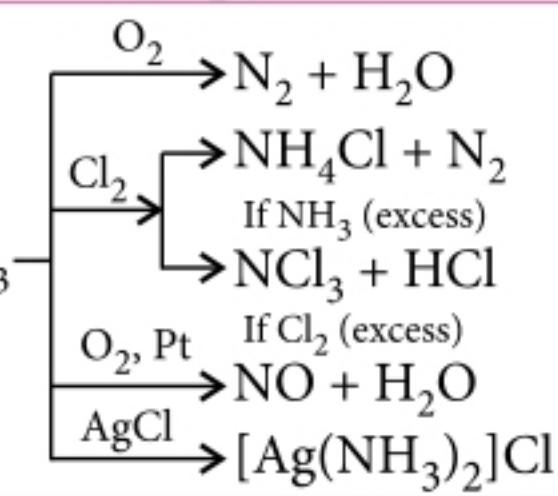
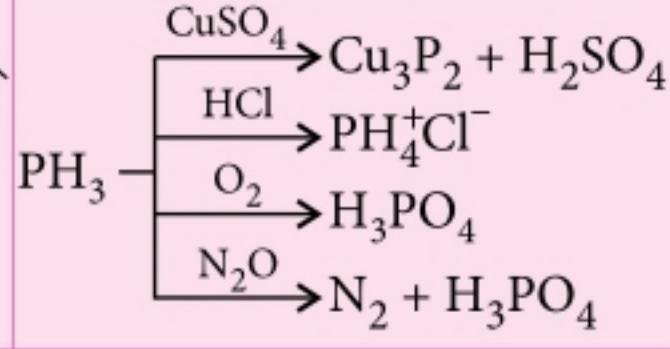
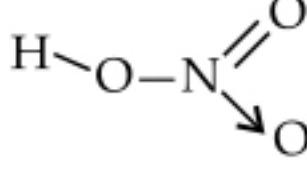
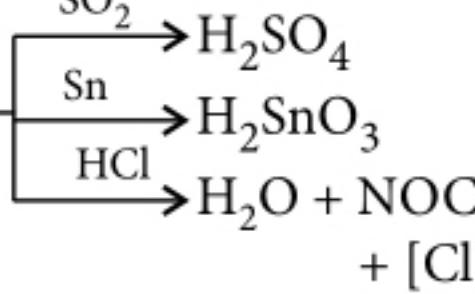
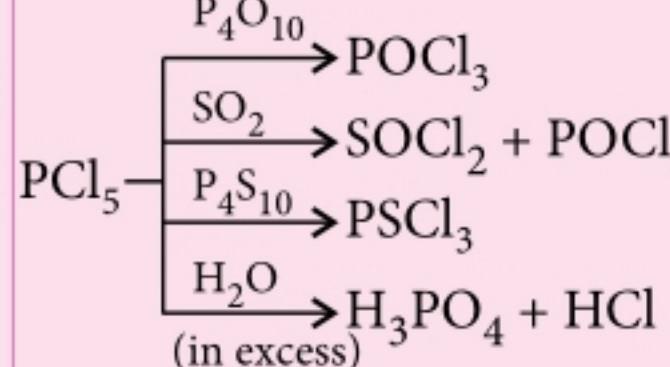
Oxoacid	Structure
Phosphinic acid (Hypophosphorous acid), H_3PO_2	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{P}-\text{H} \\ \\ \text{H} \end{array}$ Basicity = 1 O.S. of P = +1
Phosphonic acid (Orthophosphorous acid or phosphorous acid), H_3PO_3	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{P}-\text{OH} \\ \\ \text{OH} \end{array}$ Basicity = 2 O.S. of P = +3
Phosphoric acid (Orthophosphoric acid), H_3PO_4	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{P}-\text{OH} \\ \\ \text{OH} \end{array}$ Basicity = 3 O.S. of P = +5
Metaphosphoric acid (Glacial phosphoric acid), $(\text{HPO}_3)_n$	$\left(\begin{array}{c} \text{O} \\ \\ \text{P}-\text{O}-\text{OH} \\ \\ \text{O} \end{array} \right)_n$ Basicity = 1 O.S. of P = +5

Pyrophosphorous acid (diphosphorous acid), $H_4P_2O_5$	 Basicity = 2 O.S. of P = +3
Pyrophosphoric acid (diphosphoric acid), $H_4P_2O_7$	 Basicity = 4 O.S. of P = +5
Hypophosphoric acid, $H_4P_2O_6$	 Basicity = 4 O.S. of P = +4

KEY POINT

- Phosphorus pentoxide, P_4O_{10} due to its appearance as a snowy powder is called "*Flowers of Phosphorus*".
- Mixture of calcium cyanamide ($CaCN_2$) and graphite is called *nitrolim* which is used as a fertilizer.
- Tartar emetic ($C_4H_4KO_7Sb$) is potassium antimonyl tartarate which contains antimony and is used in medicine as anti-poison.
- Thomas Slag :** Mixture of $Ca_3(PO_4)_2$ and $CaSiO_3$ which is a by-product of steel industry. It contains 14-18% of P_2O_5 and 40% lime. It is used as a fertilizer.

Important Compounds of Nitrogen Family

Structure	Preparation	Properties	Uses
Ammonia (NH_3) 	$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H_f^\circ = -92.4 \text{ kJ/mol}$ (Haber's process)	NH_3 	In refrigerators, manufacturing of rayon, HNO_3 (Ostwald's process), $NaHCO_3$ (Solvay's process), nitrogenous fertilizers.
Phosphine (PH_3) 	$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3 \uparrow$	PH_3 	For production of smoke screens. Phosphine in combination with acetylene is used in preparing <i>Holme's signals</i> .
Nitric acid (HNO_3) 	$NaNO_3 + H_2SO_4 \xrightarrow{\Delta} NaHSO_4 + HNO_3$	HNO_3 	As fertilizers, explosives, perfumes, dyes and medicines. As oxidiser in rocket fuels.
Phosphorus pentachloride (PCl_5) 	P_4 (white) + $10Cl_2 \rightarrow 4PCl_5$	PCl_5 	As chlorinating and dehydrating agent.

KEY POINT

- Moist NH_3 gas is dried over quick lime, CaO . However, it cannot be dried over conc. H_2SO_4 , P_2O_5 , because being basic it forms salts with them. Anhydrous CaCl_2 also cannot be used because it forms a complex $\text{CaCl}_2 \cdot 8\text{NH}_3$ with it.
- Fe, Cr, Ni and Al become passive in conc. HNO_3 (*i.e.*, lose their normal activity) due to the formation of a thin protective layer of the oxide on the surface of the metal which prevents further action.
- Nitric acid has no action on noble metals (Au, Pt) but these metals dissolve in aqua-regia (3 vol. conc. HCl + 1 vol. conc. HNO_3) forming their respective chlorides.
- Persons working with white P (very poisonous) develop a disease known as ***Phossy jaw*** in which jaw bones decay.
- In solid state, PCl_5 exists as $[\text{PCl}_4]^+[\text{PCl}_6]^-$ in which the cation, $[\text{PCl}_4]^+$ is tetrahedral while the anion, $[\text{PCl}_6]^-$ is octahedral.

GROUP-16 ELEMENTS (OXYGEN FAMILY)

- General outer electronic configuration is ns^2np^4 , where $n = 2$ to 6.

Element	At. No.	Electronic configuration	Oxidation No.
Oxygen (O)	8	[He] $2s^22p^4$	-2, -1, +1, +2
Sulphur (S)	16	[Ne] $3s^23p^4$	-2, +2, +4, +6
Selenium (Se)	34	[Ar] $3d^{10}4s^24p^4$	-2, +2, +4, +6
Tellurium (Te)	52	[Kr] $4d^{10}5s^25p^4$	-2, +2, +4, +6
Polonium (Po)	84	[Xe] $4f^{14}5d^{10}6s^26p^4$	+2, +4, +6

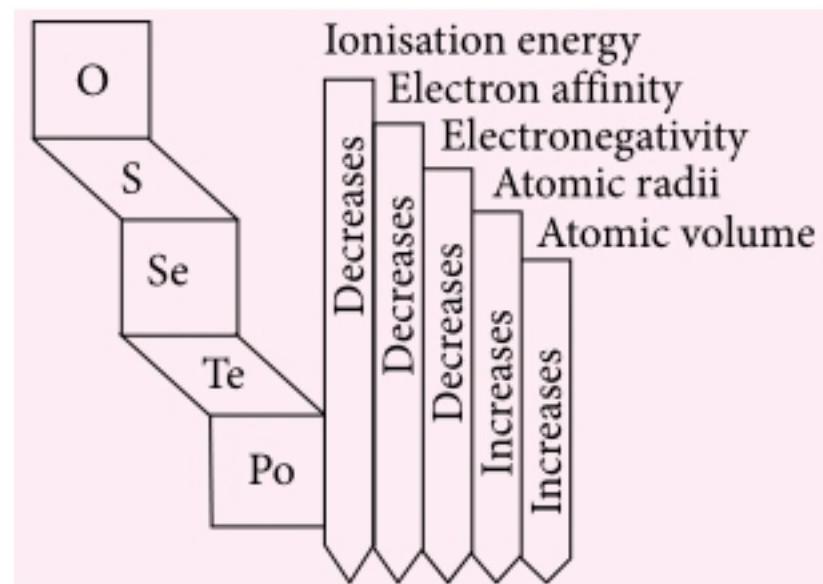
- They are collectively called as ***chalcogens***, *i.e.* ore forming elements since a large number of metal ores are either oxides or sulphides.

The first four elements of this group are non-metallic in character (O, S , Se, Te).
 Non-metals Metalloids

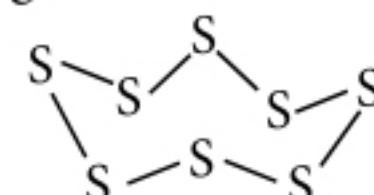
The last element of the family, polonium has metallic character and is a radioactive element with very short half-life.

KEY POINT

- Oxygen shows -2 oxidation state in general, except in O_2F_2 (+1) and OF_2 (+2).



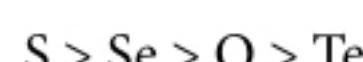
Atomicity : Oxygen is diatomic, sulphur, selenium and tellurium are octaatomic with puckered ring structure.



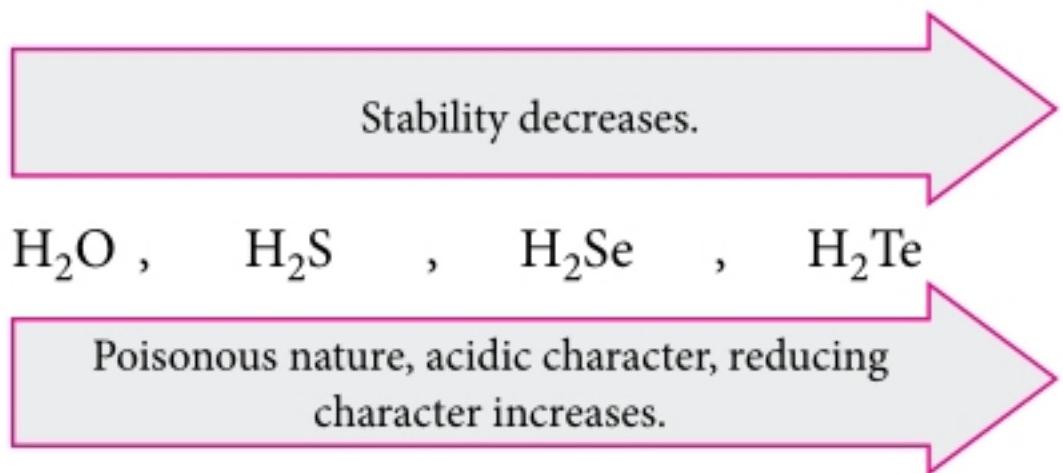
Allotropy : All the elements exhibit allotropy.

Element	Allotropic Forms
Oxygen	O_2 (dioxygen) and O_3 (ozone)
Sulphur	Rhombic (or α) sulphur S_8 , monoclinic (or β) sulphur S_8 , plastic sulphur open chain.
Selenium	Red (non-metallic) and grey (metallic)
Tellurium	Crystalline, amorphous
Polonium	α and β (both are metallic)

Catenation : Maximum in S due to highest bond strength of S—S bond.
 Order is :



Hydrides : All the elements form stable hydrides of the type H_2M where M is sp^3 hybridised.



- The weakening of $M-H$ bond with the increase in the size of M explains the acid character of hydrides.
- Volatile character first increases from H_2O to H_2S and then decreases from H_2S to H_2Te .

□ Halides :

Element	Fluorine	Chlorine	Bromine	Iodine
Oxygen	F_2O, O_2F_2	Cl_2O, ClO_2, Cl_2O_7	Br_2O	I_2O_5
Sulphur	$SF_4, SF_6, S_2F_{10}, S_2F_2$	SCl_4, SCl_2, S_2Cl_2	S_2Br_2	-
Selenium	SeF_6, SeF_4, Se_2Fe_2	$SeCl_4, SeCl_2, Se_2Cl_2$	$SeBr_4, SeBr_2^*, Se_2Br_2$	-
Tellurium	TeF_4, TeF_6, Te_2F_{10}	$TeCl_2^*, TeCl_4$	$TeBr_4, TeBr_2$	TeI_4
Polonium	PoF_6	$PoCl_4, PoCl_2$	$PoBr_4, PoBr_2$	PoI_4

* Unstable

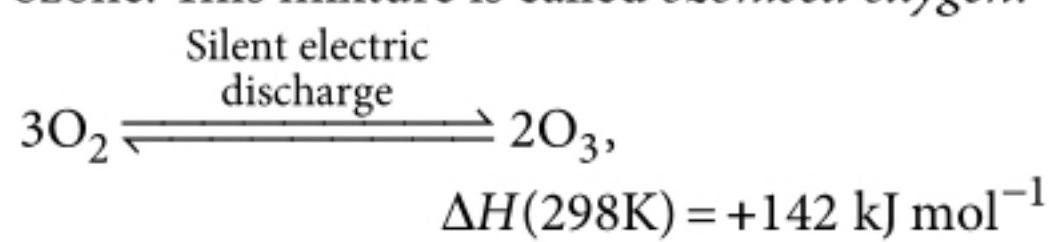
Ozone (O_3)

□ Discovered by *Van Marum*. It is an allotropic form of oxygen. It is present in small quantity in the upper layer of the atmosphere, where it is formed due to the action of ultraviolet rays on the oxygen of the air.

□ Preparation

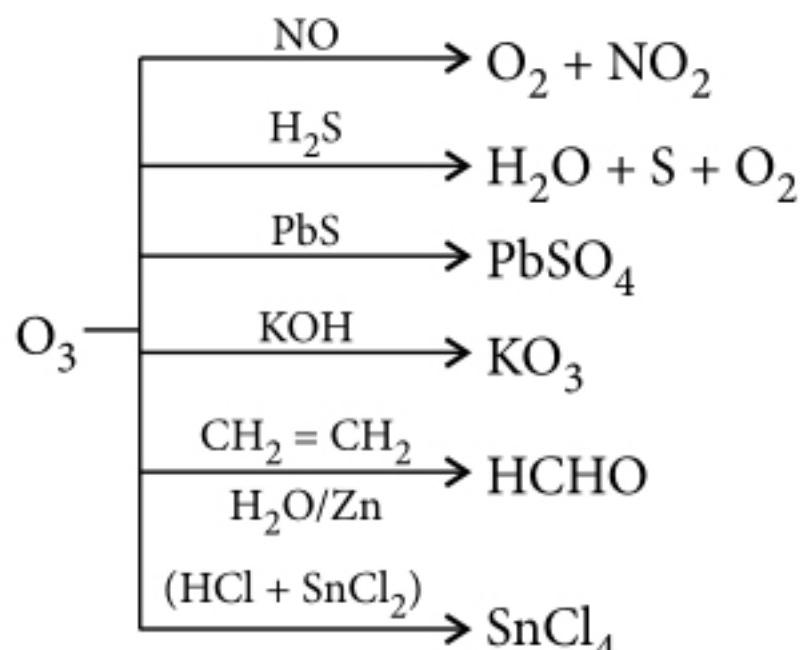
On passing silent electric discharge through dry oxygen, in an *ozoniser*, ozone is formed.

We always obtain a mixture of oxygen and ozone. This mixture is called *ozonised oxygen*.



□ Properties

Pale blue gas with characteristic strong smell, slightly soluble in water but more soluble in turpentine oil, glacial acetic acid and CCl_4 .



□ Uses

- Bleaching ivory, oils, flour.
- As germicide and disinfectant for sterilising water.
- For purifying air in crowded places.
- Manufacture of $KMnO_4$ and artificial silk.

Oxoacids of Sulphur

□ A large number of oxoacids are known in the case of sulphur either in the free state or in the form of salts or both.

KEY POINT

- Electron affinity of O is lower than that of S due to electron-electron repulsions in the small $2p$ -orbitals of O.
- S_{rhombic} changes to $S_{\text{monoclinic}}$ above $95.4^\circ C$.
- Grey hexagonal selenium is thermodynamically most stable allotropic form of Se consisting of polymeric helical chains.
- Sulphur is also called as 'brimstone'.
- H_2S is called sulphuretted hydrogen.

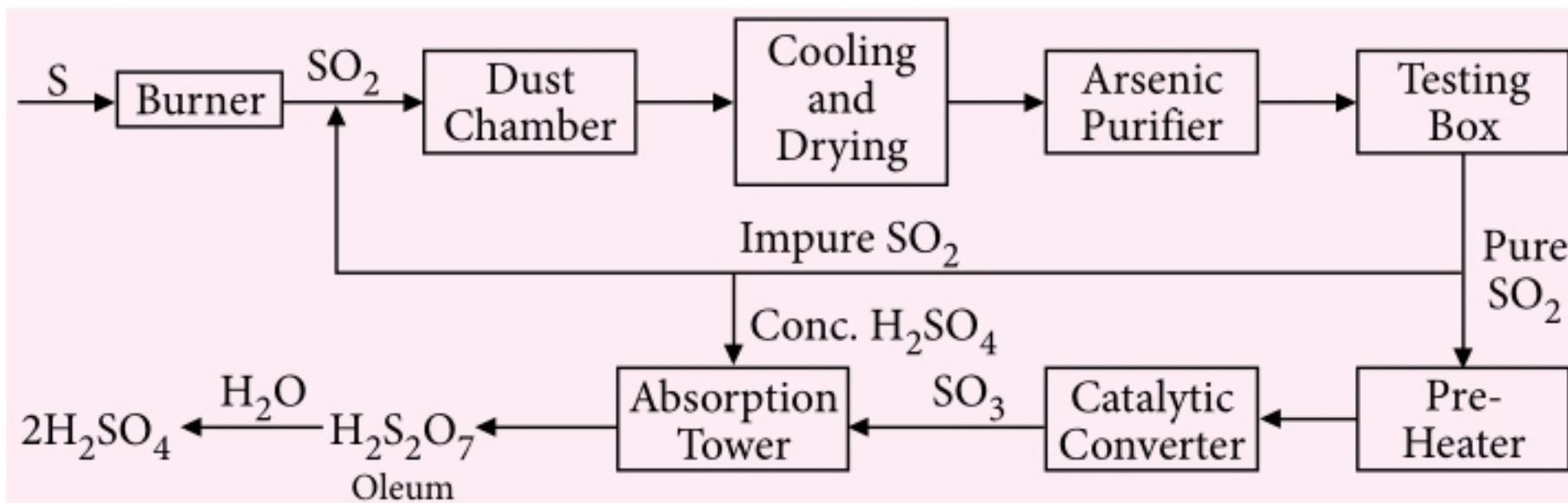
Oxoacid	Oxidation state, basicity and salt type	Structure	Properties
Sulphurous acid, H_2SO_3	$\text{S} = +4$, dibasic, and forms two series of salts, sulphites (SO_3^{2-}) and bisulphites (HSO_3^-)		- acts as reducing agent as well as oxidising agent. - exists only in solution.
Sulphuric acid (oil of vitriol), H_2SO_4	$\text{S} = +6$, dibasic and forms two series of salts, sulphates (SO_4^{2-}) and bisulphates (HSO_4^-)		- highly corrosive acts as oxidising agent and dehydrating agent.
Peroxomonosulphuric acid (Caro's acid), H_2SO_5	$\text{S} = +6$, monobasic and forms single type of salt, peroxymonosulphates (HSO_5^-)		- white, crystalline and hygroscopic solid. - powerful oxidising agent.
Peroxodisulphuric acid (Marshall's acid), $\text{H}_2\text{S}_2\text{O}_8$	$\text{S} = +6$ and forms single type of salt, peroxydisulphates ($\text{S}_2\text{O}_8^{2-}$)		- colourless, crystalline and hygroscopic solid. - strong oxidising agent.

Sulphuric acid (H_2SO_4)

□ Preparation

It is also known as *oil of vitriol* and *king of chemicals*.

○ Contact process :



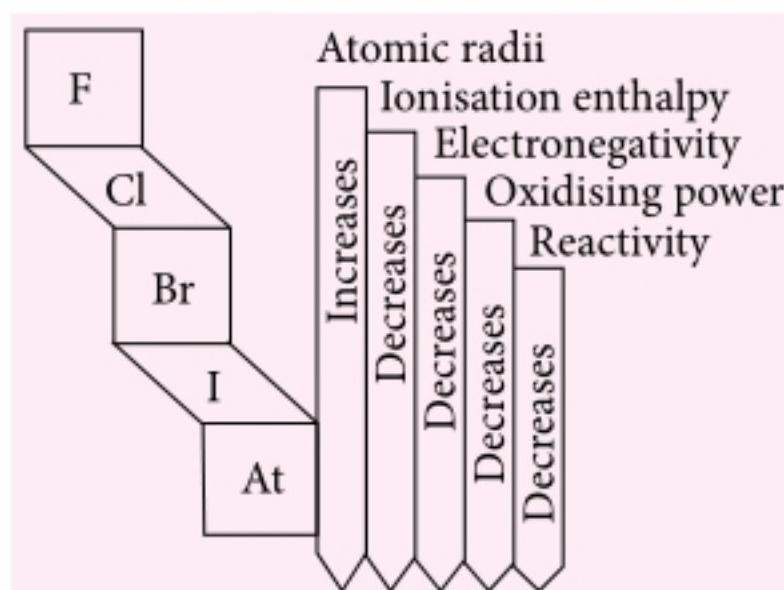
Structure	Properties	Uses																
 Sulphuric acid Sulphate ion	$\text{H}_2\text{SO}_4 \rightarrow$ <table> <tr><td>NaOH</td><td>$\rightarrow \text{NaHSO}_4 + \text{H}_2\text{O}$</td></tr> <tr><td>$2\text{NaOH}$</td><td>$\rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$</td></tr> <tr><td>$\text{Zn}$</td><td>$\rightarrow \text{ZnSO}_4 + \text{H}_2$</td></tr> <tr><td>$\text{C}_{12}\text{H}_{22}\text{O}_{11}$</td><td>$\rightarrow 12\text{C} + 11\text{H}_2\text{O}$</td></tr> <tr><td>$\text{S}_8$</td><td>$\rightarrow \text{SO}_2 + \text{H}_2\text{O}$</td></tr> <tr><td>$\text{Na}_2\text{S}$</td><td>$\rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{S}$</td></tr> <tr><td>$\text{BaCl}_2$</td><td>$\rightarrow \text{BaSO}_4 + \text{HCl}$</td></tr> <tr><td>$\text{K}_4[\text{Fe}(\text{CN})_6]$</td><td>$\rightarrow \text{K}_2\text{SO}_4 + \text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4 + \text{CO} \uparrow$</td></tr> </table>	NaOH	$\rightarrow \text{NaHSO}_4 + \text{H}_2\text{O}$	2NaOH	$\rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$	Zn	$\rightarrow \text{ZnSO}_4 + \text{H}_2$	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	$\rightarrow 12\text{C} + 11\text{H}_2\text{O}$	S_8	$\rightarrow \text{SO}_2 + \text{H}_2\text{O}$	Na_2S	$\rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{S}$	BaCl_2	$\rightarrow \text{BaSO}_4 + \text{HCl}$	$\text{K}_4[\text{Fe}(\text{CN})_6]$	$\rightarrow \text{K}_2\text{SO}_4 + \text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4 + \text{CO} \uparrow$	It is used as oxidising, dehydrating agent and for the preparation of dyes, drugs, explosives, volatile acids, etc.
NaOH	$\rightarrow \text{NaHSO}_4 + \text{H}_2\text{O}$																	
2NaOH	$\rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$																	
Zn	$\rightarrow \text{ZnSO}_4 + \text{H}_2$																	
$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	$\rightarrow 12\text{C} + 11\text{H}_2\text{O}$																	
S_8	$\rightarrow \text{SO}_2 + \text{H}_2\text{O}$																	
Na_2S	$\rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{S}$																	
BaCl_2	$\rightarrow \text{BaSO}_4 + \text{HCl}$																	
$\text{K}_4[\text{Fe}(\text{CN})_6]$	$\rightarrow \text{K}_2\text{SO}_4 + \text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4 + \text{CO} \uparrow$																	

GROUP-17 ELEMENTS (HALOGEN FAMILY)

- General outer electronic configuration is ns^2np^5 , where $n = 2$ to 6.

Element	At. No.	Electronic configuration	Oxidation No.
Fluorine (F)	9	[He]2s ² 2p ⁵	-1
Chlorine (Cl)	17	[Ne]3s ² 3p ⁵	-1, +1, +3, +5, +7
Bromine (Br)	35	[Ar]3d ¹⁰ 4s ² 4p ⁵	-1, +1, +3, +5, +7
Iodine (I)	53	[Kr]4d ¹⁰ 5s ² 5p ⁵	-1, +1, +3, +5, +7
Astatine (At)	85	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵	—

- They are collectively known as **halogens** (sea salt forming elements). Astatine is radioactive artificially prepared element.



- **Bond energy and bond length :** The bond length increases from fluorine to iodine.

	F-F	Cl-Cl	Br-Br	I-I
Bond length (\AA)	1.42	1.99	2.28	2.67
Bond energy (kJ/mol)	158.8	242.6	192.8	151.1

Due to small size the interelectronic repulsions between non-bonding electrons are high in case of fluorine which results in weakening of F-F bond.

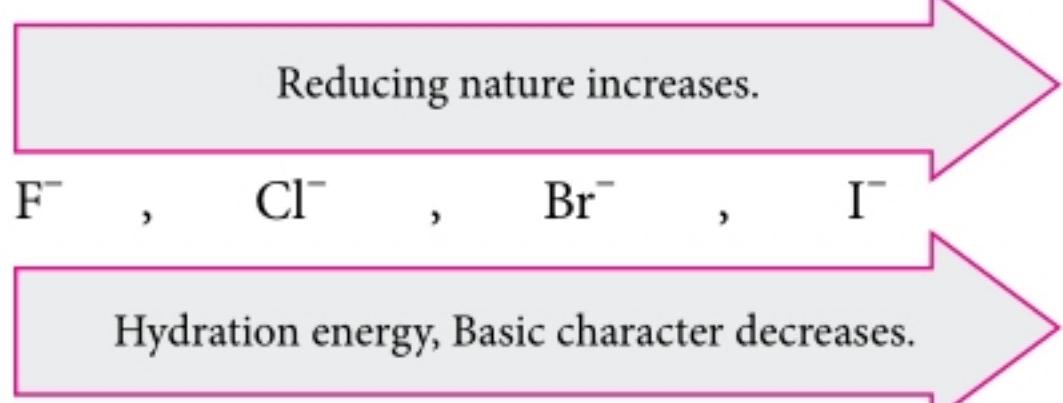
- **Solubility :** Halogens are soluble in water. The solubility of iodine in water is enhanced in presence of KI.



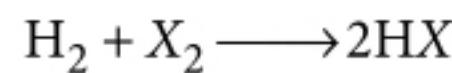
In organic solvents like CS_2 , CHCl_3 and CCl_4 , the Cl_2 , Br_2 and I_2 are more soluble and give

coloured solutions. Thus, Cl_2 gives yellow, Br_2 gives brown and I_2 gives violet solution.

- **Properties of halide ions (X^-) :** Some properties of halide ions follow the following order :



- **Hydrides (HX) :** All halogens directly combine with hydrogen to form HX known as *hydracids* or *halogen acids*.

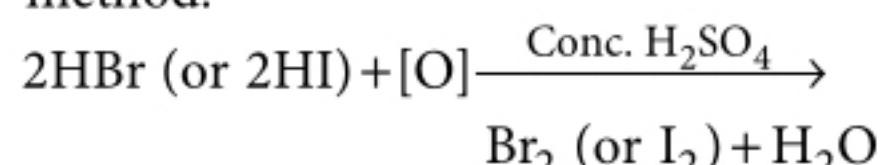


○ **Preparation :**

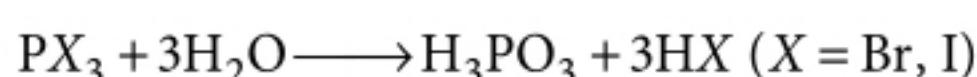
- HF and HCl can be obtained by heating fluorides and chlorides with conc. H_2SO_4 .



- HBr and HI are strongly reducing in nature and reduce conc. H_2SO_4 and thus, cannot be prepared by this method.



Hence, they are prepared by hydrolysis of phosphorus halides.



○ **Properties :**

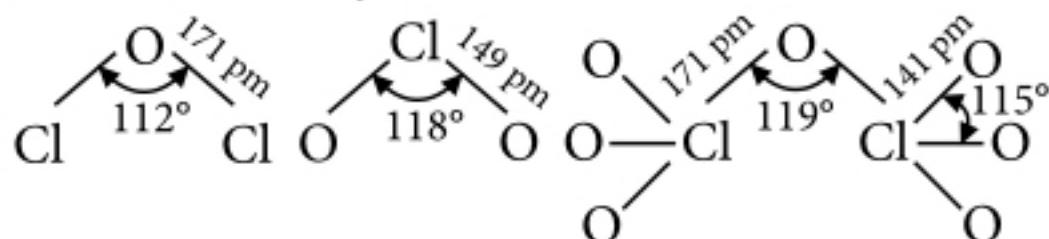
- HF is a liquid with boiling point 293 K due to intermolecular hydrogen bonding, while HCl, HBr, HI are gases.
- The boiling point follows the trend : $\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$

- **Oxides :** All form oxides of different types.

- Halogens do not combine directly with oxygen hence, they are prepared by indirect methods. They are :

OF_2	Cl_2O	Br_2O	I_2O_4
O_2F_2	ClO_2	BrO_2	I_2O_5
	ClO_3	BrO_3	I_4O_9
	Cl_2O_6		
	Cl_2O_7		

○ *Structures of some oxides :*



○ All oxides are powerful oxidising agents and decompose with explosion when heated.

□ **Oxoacids :** All form oxoacids of the type HOX , HXO_2 , HXO_3 and HXO_4 as shown below :

Name	O.N. of X	F	Cl	Br	I
Hypohalous acid, HXO	+1	HOF	HOCl	HOBr	HOI
Halous acid, HXO_2	+3	-	HClO_2	-	-
Halic acid, HXO_3	+5	-	HClO_3	HBrO_3	HIO_3
Perhalic acid, HXO_4	+7	-	HClO_4	HBrO_4	HIO_4

Thermal stability, acidic strength decreases.

HXO_4 , HXO_3 , HXO_2 , HXO

Oxidising nature increases.

Interhalogen Compounds

□ Halogens combine among themselves to form compounds known as *interhalogens* or *interhalogen compounds* of the type AX , AX_3 , AX_5 and AX_7 . Their structure and hybridisation is as follows :

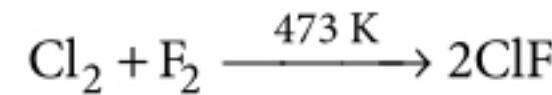
Type	Hybridisation	Shape	Structure
AX	sp^3	Linear	
AX_3	sp^3d	T-shaped	
AX_5	sp^3d^2	Square pyramidal	

AX_7	sp^3d^3	Pentagonal bipyramidal	
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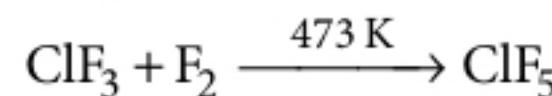
Examples : IBr , BrCl , ClF , BrF , ICl , ClF_3 , BrF_3 , ICl_3 , BrF_5 , IF_5 , IF_7 .

○ **Properties :** They are covalent, more reactive, strongly oxidising and diamagnetic in nature.

○ **Preparation :** They are prepared by direct combination of halogens.



By the action of halogens on lower interhalogen



□ **Polyhalide ions :** The ions containing more than two halogen atoms are known as *polyhalide ions*. For example,



Other examples are Br_3^- , Cl_3^- , ICl_2^- , ICl_4^- , BrF_4^- , IF_6^- , I_5^- .

□ **Pseudohalogens and pseudohalides :** The substances behaving like halogens are known as *pseudohalides*. Some examples are :

Pseudohalogens	Pseudohalides
$(\text{CN})_2$, Cyanogen	CN^- , Cyanide
$(\text{OCN})_2$, Oxycyanogen	OCN^- , Cyanate
$(\text{SCN})_2$, Thiocyanogen	SeCN^- , Selenocyanate
$(\text{SeCN})_2$, Selenocyanogen	SCN^- , Thiocyanate
	NCN^{2-} , Cyanamide
	N_3^- , Azide

KEY POINT

- Iodine also forms I^+ and I^{3+} cations due to less ionisation energy as $(\text{CH}_3\text{COO})_3\text{I}$, $\text{I}(\text{ClO}_4)_3$ and IPO_4 have been isolated.
- Because of the tendency to form hydrogen bond, metal fluorides are solvated by HF giving species of the type HF_2^- etc. $\text{KHF}_2(\text{KF}\cdot\text{HF})$, KH_2F_3 ($\text{KF}\cdot2\text{HF}$) and KH_3F_4 ($\text{KF}\cdot3\text{HF}$) are known examples.

GROUP-18 ELEMENTS (NOBLE GASES)

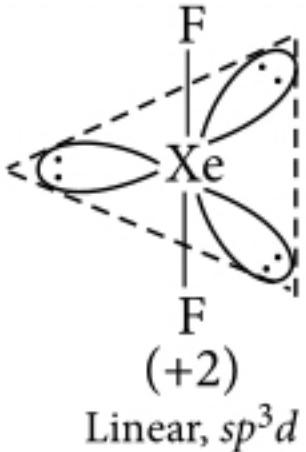
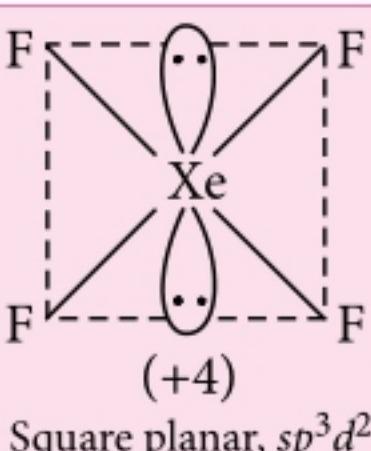
- General outer electronic configuration is $ns^2 np^6$, where $n = 2$ to 6.

Element	Atomic no.	Electronic configuration
Helium (He)	2	$1s^2$
Neon (Ne)	10	$1s^2 2s^2 2p^6$
Argon (Ar)	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Krypton (Kr)	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
Xenon (Xe)	54	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6$
Radon (Rn)	86	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$

- **Occurrence:** The relative abundance of different noble gases in the atmosphere are given below:

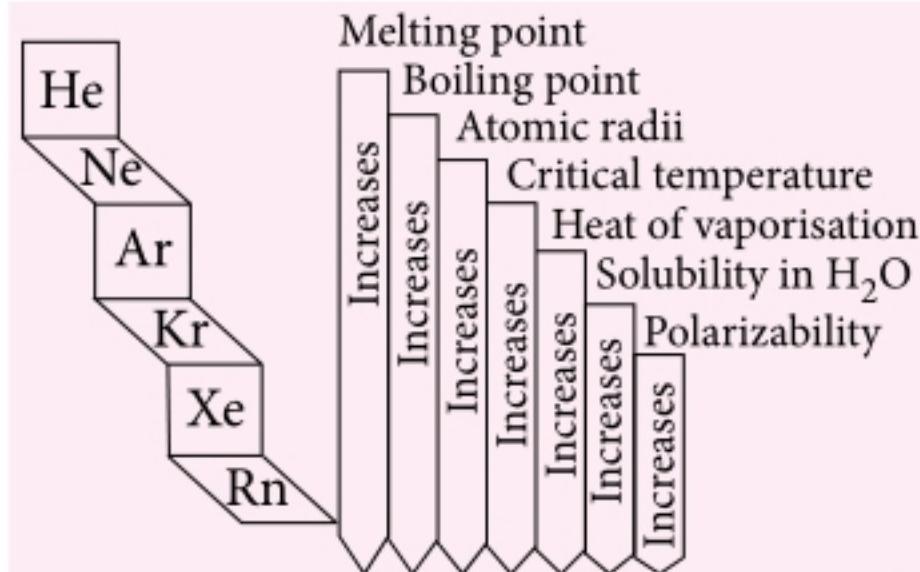
Element	Abundance in air (% by volume)
Helium (He)	5.24×10^{-4}
Neon (Ne)	1.82×10^{-3}
Argon (Ar)	0.934

□ Compounds of Xenon :

Compound	Structure	Preparation	Properties
XeF_2 (Xenon difluoride)	 (+2) Linear, sp^3d	$Xe + F_2 \xrightarrow[\text{Ni tube}]{400^\circ\text{C}} XeF_2$ $Xe + O_2F_2 \xrightarrow{118^\circ\text{C}} XeF_2 + O_2$	$\begin{array}{l} H_2 \rightarrow Xe + 2HF \\ H_2O \rightarrow Xe + 2HF + \frac{1}{2}O_2 \\ I_2 \rightarrow 2IF + Xe \\ BF_3 \rightarrow Xe + 2HF + Cl_2 \\ 2HCl \end{array}$ - Acts as fluorinating agent.
XeF_4 (Xenon tetrafluoride)	 (+4) Square planar, sp^3d^2	$Xe + F_2 \xrightarrow[\text{Ni tube}]{600^\circ\text{C}} XeF_4$	- Colourless, crystalline solid with melting point, 117.1°C . - $XeF_4 + 2H_2 \rightarrow Xe + 4HF$ - Undergoes disproportionation in water. $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$ - Gives adduct. $XeF_4 + SbF_5 \rightarrow [XeF_3]^+ [SbF_6]^-$ - Acts as fluorinating agent. - Dissolves in anhydrous HF.

Krypton (Kr)	1.14×10^{-4}
Xenon (Xe)	8.7×10^{-6}
Radon (Rn)	Trace

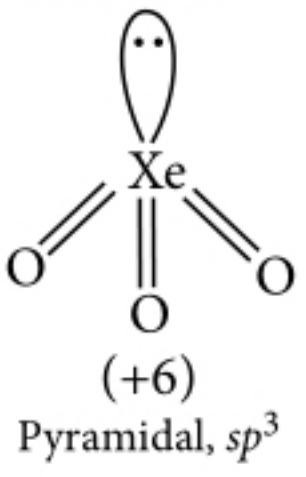
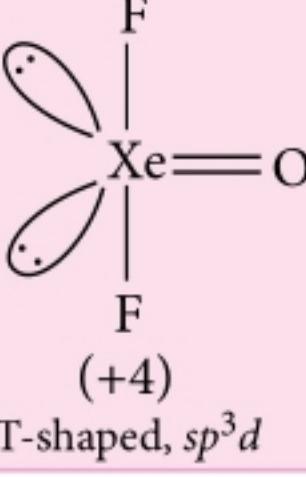
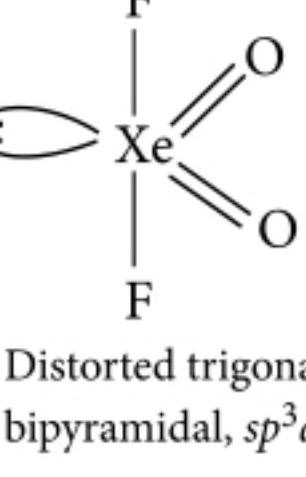
Except radon which is a radioactive element, all other noble gases occur in the elemental state in the atmosphere.



- **Liquefaction :** It is extremely difficult to liquefy inert gases due to weak van der Waals' forces of attraction among their molecules. Hence, they possess low value of critical temperature also.

KEY POINT

- **Adsorption by charcoal :** Except helium, all are adsorbed by coconut charcoal at low temperatures. The extent of adsorption increases down the group.

XeO_3 , (Xenon trioxide)	 Pyramidal, sp^3	Complete hydrolysis of XeF_4 and XeF_6 : $6\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 4\text{Xe} + 2\text{XeO}_3 + 3\text{O}_2 + 24\text{HF}$ $\text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF}$	<ul style="list-style-type: none"> - Colourless, highly explosive and powerful oxidising agent. - With water forms xenic acid. $\text{XeO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{XeO}_4$ - Undergoes disproportionation when dissolved in alkali. $2\text{XeO}_3 + 4\text{OH}^- \rightarrow \text{Xe} + \text{O}_2 + \text{XeO}_6^{4-} + 2\text{H}_2\text{O}$
XeOF_2 , (Xenon oxydifluoride)	 T-shaped, sp^3d	Partial hydrolysis of XeF_4 : $\text{XeF}_4 + \text{H}_2\text{O} \rightarrow \text{XeOF}_2 + 2\text{HF}$	<ul style="list-style-type: none"> - Unstable
XeO_2F_2 (Xenon dioxy- difluoride)	 Distorted trigonal bipyramidal, sp^3d	Partial hydrolysis of XeOF_4 or XeF_6 : $\text{XeOF}_4 + \text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 2\text{HF}$ $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$ Action of SiO_2 on XeOF_4 : $2\text{XeOF}_4 + \text{SiO}_2 \rightarrow 2\text{XeO}_2\text{F}_2 + \text{SiF}_4$	<ul style="list-style-type: none"> - Colourless solid. - Undergoes hydrolysis readily. $\text{XeO}_2\text{F}_2 + \text{H}_2\text{O} \rightarrow \text{XeO}_3 + 2\text{HF}$

□ Uses of Noble Gases

○ Helium

- Since its lifting power is 92% that of hydrogen, therefore it is used to lift weather balloons and airships.
- It is used as breathing mixture (or oxygen dilutant) for divers.
- Mixture of O_2 and He is used in the treatment of asthma.
- Used for inflating the tyres of aeroplanes.

○ Neon

- Neon lighting is used for advertising.
- It is used for filling sodium vapour lamps.
- It is also used in beacon light as safety signal for air navigators.

○ Argon

- Primarily used to create an inert atmosphere in light bulbs, welding and fluorescent bulbs.

- Used in geiger counters, as it becomes ionised in the presence of radiation.

- The ratio of ${}^{40}\text{K}$ to ${}^{40}\text{Ar}$ can be used to date the age of rocks since Ar is obtained by radioactive decay of an isotope of potassium.

○ Krypton

- The light emitted by Kr in an electric discharge tube is used for runway and approach lights in airports.

○ Xenon

- It is used in electrical flash bulbs for high speed photography.

○ Radon

- Radon is used in radiotherapy of cancer.

KEY POINT

- Noble gases have high ionisation enthalpies and almost zero electron affinity values.
- He and Ne do not form clathrate compounds while other noble gases form.

d- AND f-BLOCK ELEMENTS

- Introduction
- Properties
- Some important compounds

TIPS TO REMEMBER

d- BLOCK (TRANSITION ELEMENTS)

- Elements in which the last electron enters any one of the five *d*-orbitals of their respective
- Electronic Configuration of Transition Elements

3d-Series			4d-Series			5d-Series		
Atomic No.	Element	Electronic Configuration	Atomic No.	Element	Electronic Configuration	Atomic No.	Element	Electronic Configuration
21	Sc	[Ar]3d ¹ 4s ²	39	Y	[Kr]4d ¹ 5s ²	57	La	[Xe]5d ¹ 6s ²
22	Ti	[Ar]3d ² 4s ²	40	Zr	[Kr]4d ² 5s ²	72	Hf	[Xe]4f ¹⁴ 5d ² 6s ²
23	V	[Ar]3d ³ 4s ²	41	Nb	[Kr]4d ⁴ 5s ¹	73	Ta	[Xe]4f ¹⁴ 5d ³ 6s ²
24	Cr	[Ar]3d ⁵ 4s ¹	42	Mo	[Kr]4d ⁵ 5s ¹	74	W	[Xe]4f ¹⁴ 5d ⁴ 6s ²
25	Mn	[Ar]3d ⁵ 4s ²	43	Tc	[Kr]4d ⁵ 5s ²	75	Re	[Xe]4f ¹⁴ 5d ⁵ 6s ²
26	Fe	[Ar]3d ⁶ 4s ²	44	Ru	[Kr]4d ⁷ 5s ¹	76	Os	[Xe]4f ¹⁴ 5d ⁶ 6s ²
27	Co	[Ar]3d ⁷ 4s ²	45	Rh	[Kr]4d ⁸ 5s ¹	77	Ir	[Xe]4f ¹⁴ 5d ⁷ 6s ²
28	Ni	[Ar]3d ⁸ 4s ²	46	Pd	[Kr]4d ¹⁰ 5s ⁰	78	Pt	[Xe]4f ¹⁴ 5d ⁹ 6s ¹
29	Cu	[Ar]3d ¹⁰ 4s ¹	47	Ag	[Kr]4d ¹⁰ 5s ¹	79	Au	[Xe]4f ¹⁴ 5d ¹⁰ 6s ¹
30	Zn	[Ar]3d ¹⁰ 4s ²	48	Cd	[Kr]4d ¹⁰ 5s ²	80	Hg	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²

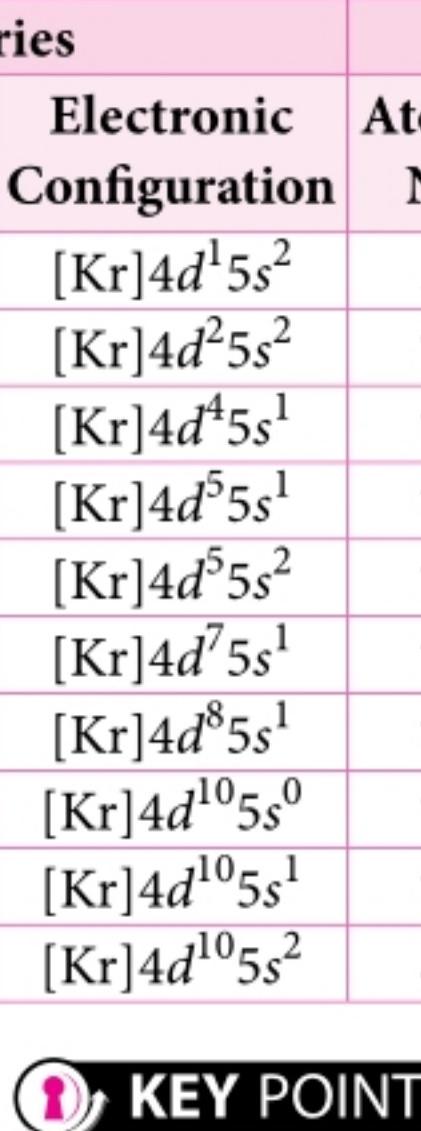
□ Metallic Character

- Transition metals can lose valence electrons and form cations $M \longrightarrow M^{n+} + ne^-$.
- They have *hcp*, *ccp* and *bcc* lattices, characteristic of true metals.
- Except Hg, they are solids at room temperature and are dense (density of osmium 22.6 g/cm³), lustrous, malleable, ductile, thermal and electrical conductors. There is gradual decrease in electropositive character from left to right.

- **Ionisation energies** : The ionisation energy increases with the increase in the atomic number but not in regular manner. The *I.E.* of 5d-elements are higher than those of the 4d- and 3d-elements due to greater effective nuclear charge which in turn is due to poor shielding of nucleus by 4f electrons.

penultimate shells are known as *transition elements*.

- Their general electronic configuration is $(n-1)d^{1-10}ns^{0-2}$ where n is the outermost shell. When electrons are filled, *ns*-orbital is filled first then $(n-1)d$ -orbital and during oxidation, *ns* electrons are lost first then $(n-1)d$ -electrons.
- The presence of unpaired and unfilled *d*-orbitals favours *covalent bonding*.



KEY POINT

- Formation of Ni^{4+} requires 11.29 kJ mol⁻¹ and formation of Pt^{4+} requires 9.36 kJ mol⁻¹ of energy. Thus, K_2PtCl_6 is well known whereas the corresponding nickel compound is not known.

□ Electrode Potential (E°)

$E^\circ(M^{n+}/M)$ is governed by three factors :

- Heat of sublimation
- Heat of ionisation
- Heat of hydration

For the 3d-transition metals the $E^\circ(M^{2+}/M)$ values are :

V	Cr	Mn	Fe	Co	Ni	Cu
-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	0.34 (Volts)

The irregular trend is due to variation in ionisation energies and sublimation energies. Except copper 3d-elements are good reducing agents but weaker than s-block elements.

□ Magnetic properties : They are

- *Paramagnetic* : Paramagnetic substances are weakly attracted by an applied magnetic field. This is due to the presence of unpaired electrons in *d*-orbitals. Paramagnetic character increases with the number of unpaired electrons.
- *Diamagnetic* : Diamagnetic substances are repelled by an applied magnetic field.
- *Ferromagnetic* : In this case permanent magnetic moment is acquired by substance. e.g., Fe.
- Magnetic moment is given by
 $\mu = \sqrt{n(n+2)}$ B.M where n = number of unpaired electrons and B.M = Bohr Magneton (unit of magnetic moment).

□ Catalytic properties : The transition metals and their compounds behave as catalyst due to

- The presence of partially filled *d*-orbitals and various oxidation states.
- The formation of intermediate complex with reactants and thus lowering the energy of activation.
- Their rough surface area which provides active sites for adsorption of reactant molecules. e.g., Iron in the preparation of NH_3 (Haber's Process).
 - Finely divided nickel for hydrogenation.
 - Pt or V_2O_5 in the preparation of H_2SO_4 .

□ Complex formation : They are well known to form a large number of complex compounds mainly due to

- Small atomic size and higher nuclear charge.
- Presence of partly filled or vacant orbitals e.g., $\text{K}_4[\text{Fe}(\text{CN})_6]$.

□ Oxidation States

- In different types of compounds, transition metals exhibit different oxidation states.

- The highest oxidation state is exhibited in fluorides and oxides.
- In lower oxidation state, the compounds formed are ionic and in higher oxidation state, they are covalent in nature.
- The highest oxidation state shown by any transition metal is +8. Ru (4d series) and Os (5d series) show +8 oxidation state.

Element	Oxidation states
Sc	+3
Ti	(+2), +3, +4
V	+2, +3, +4, +5
Cr	+2, +3, +4, +5, +6
Mn	+2, +3, +4, (+5), +6, +7
Fe	+2, +3, (+4), (+6)
Co	+2, +3, +4
Ni	+2, (+3), (+4)
Cu	+1, +2
Zn	+2

Very rare oxidation states are given in brackets.

 **KEY POINT**

- Transition metals show zero oxidation state in some complexes e.g., in $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$; Ni and Fe have zero oxidation state.
- Interstitial compounds :** The empty space present in a crystal lattice is known as *interstitial space*. The non metal atoms due to their small size (e.g., H, B, N, C etc.) when occupy such place, the resulting compound is known as *interstitial compound*. Such compounds are hard and rigid e.g., cast iron and steel.

□ Coloured Ions

- The colour exhibited by transition metal ions is due to the presence of unpaired electrons in *d*-orbitals which permits the *d-d* excitation of electrons.
- Colour of a complex depends on the *metal*, its *oxidation state* and its *ligands*.
 e.g., $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ is pale blue,
 $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is dark blue.

Some Important Compounds of Transition Elements

Compounds	Preparation	Physical properties	Uses
Potassium dichromate ($K_2Cr_2O_7$)	From sodium dichromate (obtained from chromite ore). $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$	Orange red, crystalline solid, oxidising agent, melting point, $398^\circ C$	In dyeing, photography and leather industry.
Potassium permanganate ($KMnO_4$)	From potassium manganate (obtained from pyrolusite). $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$	Deep purple, crystalline solid, oxidising agent, melting point, $240^\circ C$	As disinfectant, germicide, Baeyer's reagent (alkaline $KMnO_4$).

f-BLOCK (INNER-TRANSITION ELEMENTS)

- The block consists of two series of elements known as *lanthanides* and *actinides*.
- The general outer electronic configuration of the f-block elements is $(n - 2)f^{1-14}(n - 1)d^{0-1}ns^2$.
- For lanthanides, n is 6 while its value is 7 for actinide series.

Lanthanides

- General outer electronic configuration is $4f^{1-14}5d^{0-1}6s^2$
- The fifteen elements from lanthanum (At. no. 57) to lutetium (At. no. 71) are known as *lanthanides* or *rare earths* (because they were obtained as earths (oxides) from relatively rare minerals).

Element	Atomic number	Electronic configuration	Oxidation states
La	57	[Xe] $5d^16s^2$	+3
Ce	58	[Xe] $4f^15d^16s^2$	+3, +4
Pr	59	[Xe] $4f^36s^2$	+3, (+4)
Nd	60	[Xe] $4f^46s^2$	(+2), +3, +4
Pm	61	[Xe] $4f^56s^2$	+3
Sm	62	[Xe] $4f^66s^2$	(+2), +3
Eu	63	[Xe] $4f^76s^2$	+2, +3
Gd	64	[Xe] $4f^75d^16s^2$	+3
Tb	65	[Xe] $4f^96s^2$	+3, +4
Dy	66	[Xe] $4f^{10}6s^2$	+3, (+4)

Ho	67	[Xe] $4f^{11}6s^2$	+3
Er	68	[Xe] $4f^{12}6s^2$	+3
Tm	69	[Xe] $4f^{13}6s^2$	(+2), +3
Yb	70	[Xe] $4f^{14}6s^2$	+2, +3
Lu	71	[Xe] $4f^{14}5d^16s^2$	+3

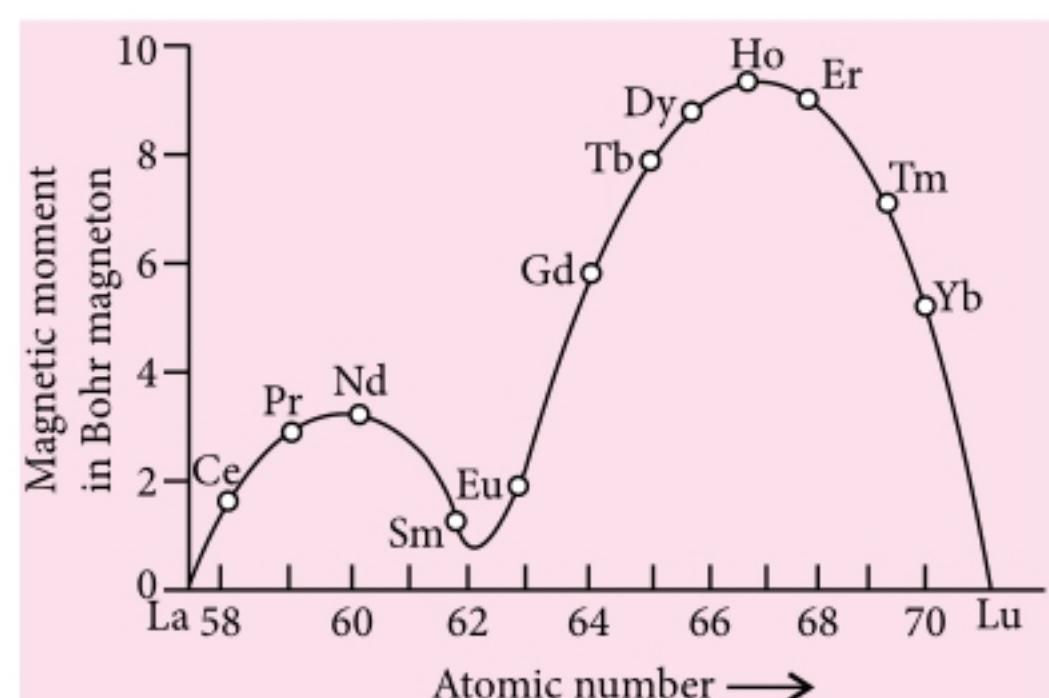
Very rare oxidation states are given in brackets.

- **Oxidation state :** The common oxidation state of lanthanides is +3 but some elements also exhibit +2 and +4 oxidation states in which they leave behind stable ions. e.g.,
 Eu^{2+} : [Xe] $4f^7$, Yb^{2+} : [Xe] $4f^{14}$
 Ce^{4+} : [Xe] $4f^0$, Tb^{4+} : [Xe] $4f^7$
- **Magnetic properties :** Magnetic properties have *spin* and *orbit* contributions (contrast to "spin only" of transition metals). Hence, magnetic moment is given by the formula

$$\mu = \sqrt{4S(S+1) + L(L+1)}$$

where L = orbital quantum number, S = spin quantum number.

Trend in magnetic moment is shown by graph:



KEY POINT

- An aqueous solution of Ce^{4+} is a good oxidising agent.
- Eu^{2+} and Yb^{2+} can exist in aqueous solution and are good reducing agents.
- All lanthanide ions with the exception of La^{3+} , Lu^{3+} and Ce^{4+} are paramagnetic in nature.

- **Lanthanide contraction :** It is the decrease in size of atoms and ions with increase in atomic number in lanthanide series.
 - **Consequences of lanthanide contraction :**
 - There is decrease in basic strength of oxides and hydroxides with decrease in the size from La to Lu.
 - Similar chemical properties.
 - The electronegativity of trivalent ions increases slightly from La to Lu.
 - There is small increase in standard electrode potential values from La to Lu.
- **Colour :** The species containing unpaired electrons are coloured and so is the case with lanthanide ions. The $f-f$ transitions are possible due to absorption of light from the visible region.
- **Reactivity :** Due to their low values of ionisation energies, the lanthanides are very reactive.
- **Alloys :** They form alloy especially with iron. e.g., MISCH METAL (rare earths 94-95%, iron 5% and S, C, Ca, Al in traces).

Actinides

- General outer electronic configuration is $5f^{1-14} 6d^{0-1} 7s^2$.

Element	Atomic no.	Electronic configuration	Oxidation states
Ac	89	[Rn] $6d^1, 7s^2$	+3
Th	90	[Rn] $6d^2, 7s^2$	+3, +4
Pa	91	[Rn] $5f^2, 6d^1, 7s^2$	+3, +4, +5
U	92	[Rn] $5f^3, 6d^1, 7s^2$	+3, +4, +5, +6
Np	93	[Rn] $5f^4, 6d^1, 7s^2$	+3, +4, +5, +6, +7
Pu	94	[Rn] $5f^6, 7s^2$	+3, +4, +5, +6, +7

Am	95	[Rn] $5f^7, 7s^2$	+3, +4, +5, +6
Cm	96	[Rn] $5f^7, 6d^1, 7s^2$	+3, +4
Bk	97	[Rn] $5f^9, 7s^2$	+3, +4
Cf	98	[Rn] $5f^{10}, 7s^2$	+3
Es	99	[Rn] $5f^{11}, 7s^2$	+3
Fm	100	[Rn] $5f^{12}, 7s^2$	+3
Md	101	[Rn] $5f^{13}, 7s^2$	+3
No	102	[Rn] $5f^{14}, 7s^2$	+3
Lr	103	[Rn] $5f^{14}, 6d^1, 7s^2$	+3

- **Actinide contraction** is similar to lanthanide contraction due to poor shielding by $5f$ electrons.
- The ions having 2 to 6 electrons in $5f$ -orbitals are coloured, both in crystalline and in aqueous solution, due to $f-f$ transition.
- Ions with $5f^0$, $5f^7$ and $5f^{14}$ configurations are colourless.
- They have higher tendency to form complex compounds.
- **Oxidation state :** The common oxidation state is +3 but other oxidation states are also exhibited by actinides, the maximum being +7.

COORDINATION COMPOUNDS

- Introduction
- Werner's coordination theory
- Isomerism
- Bonding in coordination compounds
- Importance of coordination compounds

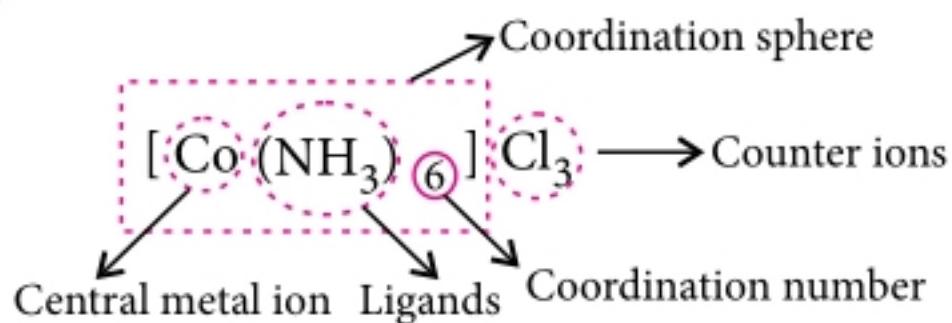
TIPS TO REMEMBER

- Difference between a double salt and coordination compound :

Coordination compound	Double salt
A coordination compound may or may not be ionic but the complex part always contains coordinate bonds.	A double salt is ionic compound and does not contain any coordinate bond.

A coordination compound (complex) retains its identity in the solution. e.g., Mohr's salt $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ solution.
e.g., $\text{K}_4[\text{Fe}(\text{CN})_6]$

Important Terms



- **Ligand** : An ion or a molecule that can have an independent existence and can donate a pair of electrons. It can be negative ion, neutral molecule or positive cation (though rare in nature).
- **Denticity** : It is the number of such ligating groups.
 - *Unidentate* : Which binds to a metal through a single point of attachment. e.g., NH_3 , Br^- , etc.
 - *Bidentate* : Which binds to a metal through two points. e.g., Ethylenediamine (*en*), oxalate (*ox*), etc.
 - *Polydentate* : Several donor atoms are present in one molecule. e.g., EDTA is hexadentate i.e., 6 donor atoms are present in it.
- **Chelate complex** : It is formed when a bi or polydentate ligand uses two or more donor atoms to bind to one metal atom.
 - Most common elements to act as donor atoms are N, P, O, S, halides and C (in organometallic compounds).
- **Ambidentate ligands** : Can ligate through two different atoms. e.g., NO_2^- , SCN^- , etc.

$$M \leftarrow \text{NO}_2, \quad M \leftarrow \text{ONO}$$

$$M \leftarrow \text{SCN}, \quad M \leftarrow \text{NCS}$$
- **Coordination number** : It is the number of ligand donor atoms to which the metal is directly bonded.
- **Effective atomic number (EAN)** : It can be obtained from the following simple expression.

$$\text{EAN} = Z - \text{O.N.} + 2(\text{C.N.})$$

where Z = Atomic number, O.N. = Oxidation number, C.N. = Coordination number of central metal atom.

- **Homoleptic complexes** : Metal bound to only one type of donor groups. e.g., $[\text{Co}(\text{NH}_3)_6]^{3+}$.
- **Heteroleptic complexes** : Metal bound to more than one type of donor groups. e.g., $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.

Rules for IUPAC Nomenclature

- Name the cation, then anion.
- Non ionic compounds are given one-word name.
- Naming of ligands :
 - Ligands are named first and central atom last.
 - Ligands are named in alphabetical order.
 - Neutral ligands are named the same as the molecule (except aqua and amine).
 - Anionic ligands are named by adding *-o* to the stem of the name (chloride becomes chlorido).
 - The ligand name is proceeded by a Latin or a Greek prefix to indicate how many are present, *di-*, *tri-*, *tetra-*, *penta-*, *hexa-*.
- In a neutral or cationic complex, the name of the central metal atom is followed by its oxidation number in roman numerals in parentheses.
- In case of bridging ligand the prefix μ is written before the name of the ligand.

Werner's Coordination Theory

Werner was able to explain the nature of bonding in complexes.

According to Werner's theory metals have two types of linkages (valencies) :

- **Primary linkages** : Which are satisfied by the negative ions, ionisable and their number is equal to the O.N. of central metal atom. They are always represented by dotted lines.
- **Secondary linkages** : Which are satisfied by the negative, neutral or a positive species (ligands) and their number is equal to the coordination number of the central metal atom. These are non-ionisable and represented by complete lines.

Isomerism

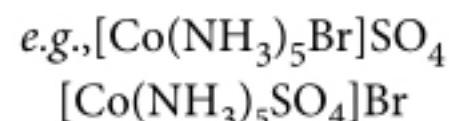
- Isomers are the compounds with the same molecular formula but different arrangements of atoms. They have different properties.

Structural isomerism

Coordination compounds having different ligands within their coordination spheres.

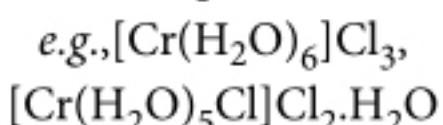
Ionisation isomerism

Complexes that give different ions in solution.



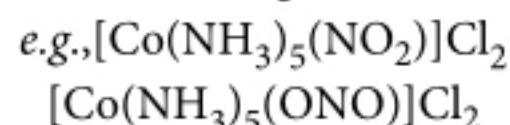
Hydrate/Solvate isomerism

Complexes that differ in number of water molecules present as ligands (inside the coordination sphere) and as free molecules (outside the coordination sphere).



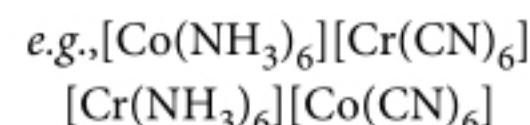
Linkage isomerism

Complexes that differ in the atom of a ligand directly bonded to the metal atom, shown by complexes containing ambidentate ligands.



Coordination isomerism

Occurs when both positive and negative ions are complex ions and two isomers differ in ligand's distribution in two complex ions.



Stereoisomerism

Coordination compounds having different positions and arrangements of ligands in space.

Geometrical isomerism

Arises in heteroleptic complexes due to different possible geometric arrangement of the ligand.

Optical isomerism

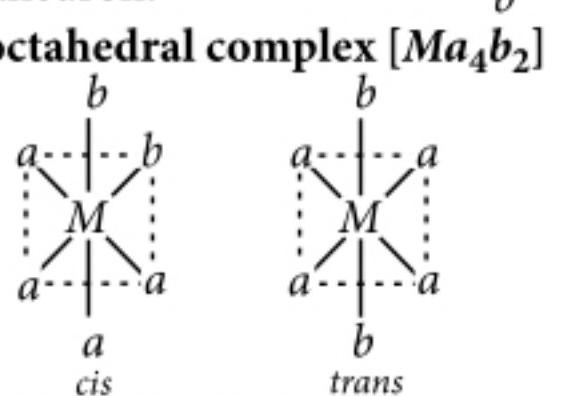
Occurs when a complex is represented by two different structures which are non-superimposable mirror images of each other called enantiomers.

In octahedral complex $[\text{Ma}_3\text{b}_3]$

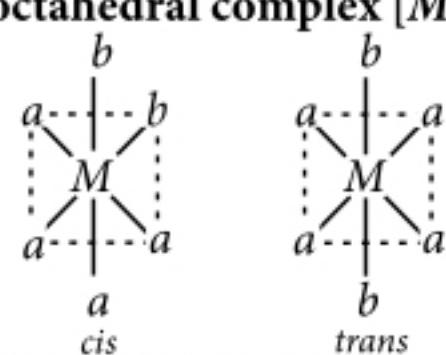
Facial (fac) : 3 donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face.



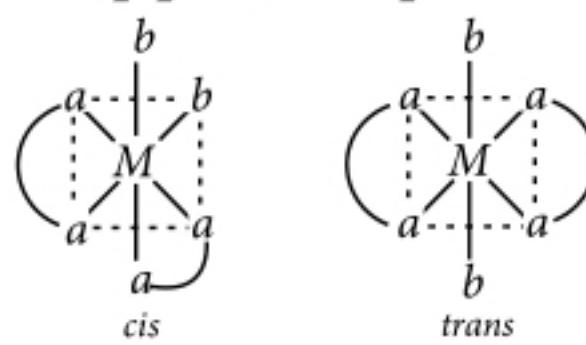
Meridional (mer) : When the positions are around the meridian of the octahedron.



In octahedral complex $[\text{Ma}_4\text{b}_2]$

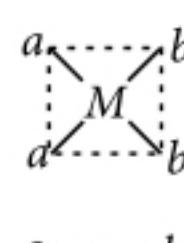


In octahedral complex $[\text{M}(aa)_2\text{b}_2]$ or $[\text{M}(aa)_2\text{bc}]$

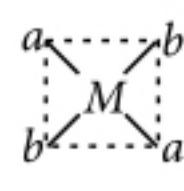


In square planar complex $[\text{Ma}_2\text{b}_2]$

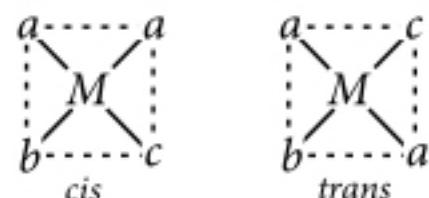
cis : 2 same ligands are arranged adjacent to each other.



trans : 2 same ligands are arranged opposite to each other.



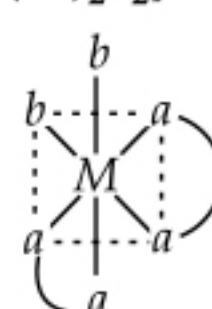
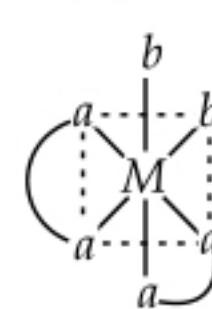
In square planar complex $[\text{Ma}_2\text{bc}]$



In square planar complex $[\text{Mabcd}]$

These isomers are obtained by selecting 1 ligand, (a) and then placing the remaining 3 ligands (b, c and d), one by one, trans to ligand (a).

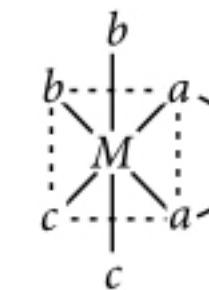
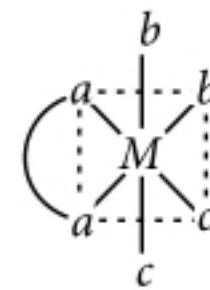
Optical isomerism in $[\text{M}(aa)_2\text{b}_2]$



$[\text{M}(aa)_3]$



$[\text{M}(aa)\text{b}_2\text{c}_2]$



dextro (d): Rotates plane of polarised light to right.

laevo (l) : Rotates plane of polarised light to left.

Bonding in Coordination Compounds

- Valence bond theory (VBT)** : Features of this theory are :
- Uses hybrid orbitals to hold the donated electron pairs for the formation of the coordinate bonds.
 - Can explain the structure and magnetic properties.

Coordination number	Type of hybridisation	Geometry	Examples
2	sp	Linear	$[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{Ag}(\text{CN})_2]^-$
3	sp^2	Trigonal planar	$[\text{HgI}_3]^-$
4	sp^3	Tetrahedral	$\text{Ni}(\text{CO})_4$, $[\text{NiX}_4]^{2-}$, $[\text{ZnCl}_4]^{2-}$, $[\text{CuX}_4]^{2-}$, where $X = \text{Cl}^-, \text{Br}^-, \text{I}^-$
	dsp^2	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ $[\text{Ni}(\text{NH}_3)_4]^{2+}$

5	dsp^3	Trigonal bipyramidal	$\text{Fe}(\text{CO})_5$, $[\text{CuCl}_5]^{3-}$
	sp^3d	Square pyramidal	$[\text{SbF}_5]^{2-}$
6	d^2sp^3	Octahedral (Inner orbital)	$[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$
	sp^3d^2	Octahedral (Outer orbital)	$[\text{FeF}_6]^{3-}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$

Inner orbital complexes	Outer orbital complexes
Involves inner d -orbitals <i>i.e.</i> , $(n - 1)d$ -orbitals.	Involves outer d -orbitals. <i>i.e.</i> , nd -orbitals.
Low spin complexes	High spin complexes
Have less or no unpaired electrons. <i>e.g.</i> , $[\text{Co}(\text{NH}_3)_6]^{3+}$,	Have large number of unpaired electrons. <i>e.g.</i> , $[\text{MnF}_6]^{3-}$, $[\text{CoF}_6]^{3-}$
$[\text{Co}(\text{CN})_6]^{4-}$	

Applications of VBT to Some Complexes

S. no.	Atom/ion complex	Configuration	Oxidation state of metal	Hybridisation and geometry	No. of unpaired electrons	Magnetic behaviour
1.	$\text{Ni}^{2+} (d^8)$		+2		2	Paramagnetic
	$[\text{NiCl}_4]^{2-}$	 sp^3	+2	sp^3 , Tetrahedral	2	Paramagnetic
	$[\text{Ni}(\text{CN})_4]^{2-}$	 Rearrangement dsp^2	+2	dsp^2 , Square planar	0	Diamagnetic
2.	$\text{Mn}^{2+} (d^5)$		+2		5	Paramagnetic
	$[\text{Mn}(\text{CN})_6]^{4-}$	 Rearrangement d^2sp^3	+2	d^2sp^3 (Inner), Octahedral	1	Paramagnetic
	$[\text{MnCl}_4]^{2-}$	 sp^3	+2	sp^3 , Tetrahedral	5	Paramagnetic

3.	$\text{Cu}^{2+}(d^9)$		+2		1	Paramagnetic
	$[\text{CuCl}_4]^{2-}$	 sp^3	+2	sp^3 , Tetrahedral	1	Paramagnetic
	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	 dsp^2 One electron is shifted from 3d to 4p-orbital	+2	dsp^2 , Square planar	1	Paramagnetic
4.	$\text{Fe}^0(d^6s^2)$		0		4	Paramagnetic
	$[\text{Fe}(\text{CO})_5]$	 Rearrangement dsp^3	0	dsp^3 , Trigonal bipyramidal	0	Diamagnetic

□ Limitations of VBT

- It does not offer an explanation for the existence of inner-orbital and outer-orbital complexes.
- It cannot explain colour and spectra.
- The thermodynamic or kinetic stabilities of coordination compounds are not quantitatively interpreted.

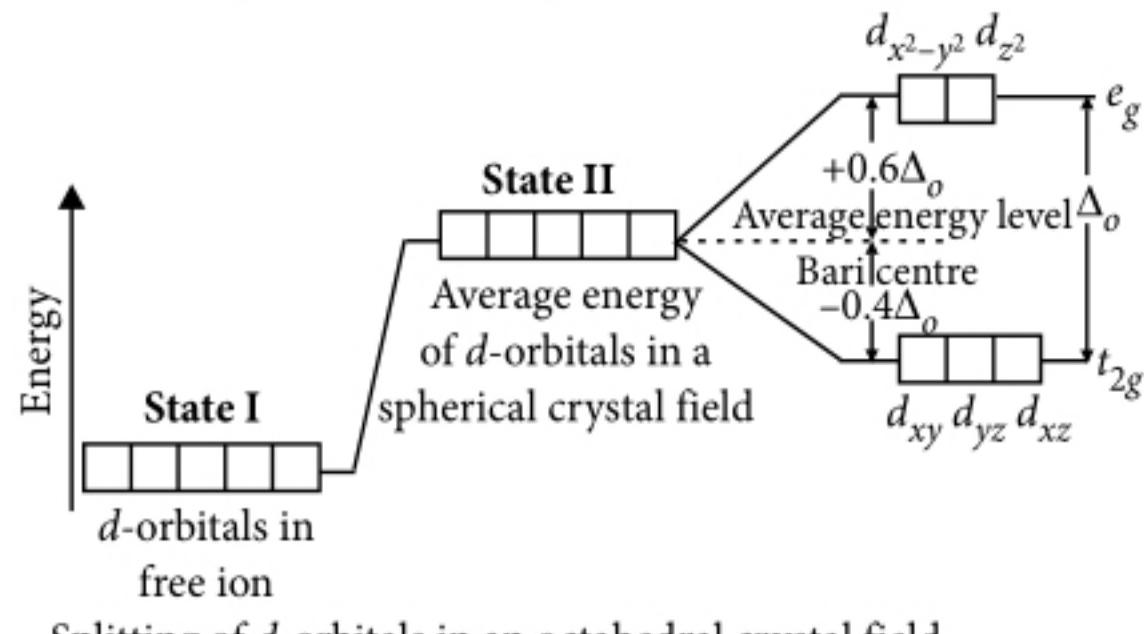
Crystal Field Theory

□ Crystal field theory (CFT) was proposed by *Bethe* and *Ven Vleck*. It gives satisfactory explanation for the properties and bonding in coordination compounds.

The main points of this theory are :

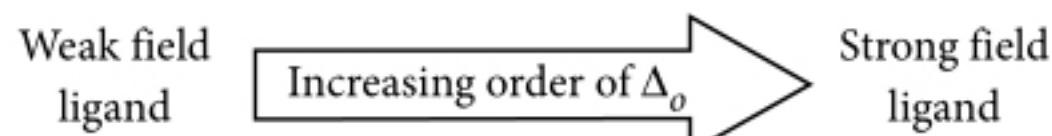
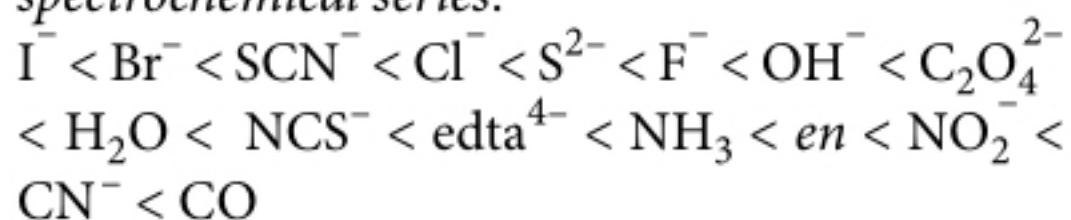
- The attraction between the central metal and ligands in the complexes is considered to be purely electrostatic. Thus bonding in the complex may be ion-ion attraction or ion dipole attraction.
- Ligands are treated as points of negative charges.
- There is no interaction between metal orbitals and ligand orbitals.
- The *d*-orbitals present in metal have the same energy in the free state. This is called degenerate state of *d*-orbitals. But, when a complex is formed the ligands destroy the degeneracy of these orbitals. This effect is known as *Crystal field splitting* of *d*-orbitals.

It accounts for both the colour and the magnetic properties of complexes. It is based on *d*-orbital energy level splitting.



Spectrochemical Series

□ When the ligands are arranged in order of the magnitude of crystal field splitting, the arrangement, thus, obtained is called *spectrochemical series*.



□ **Effect of strong field ligands and weak field ligands :** Strong field ligands force the electrons of central metal for pairing and the complex formed is known as *low spin complex* while weak field ligands do not force the electrons of central atom for pairing and the complex formed is known as *high spin complex*.

For example : In $[\text{Ni}(\text{CN})_4]$, CN^- is a strong field ligand which forces electrons of Ni^{2+} for pairing.

□ The size of the Δ_o depends on :

- Position of transition metal,
 - Δ_o increases down the group.
 - Δ_o of II transition series is 50% higher than I transition series.
 - Δ_o of III transition series is 25% higher than II transition series.
- The oxidation state of the metal,
 - Δ_o is greater for M^{3+} than for M^{2+} .
- The row of the metal in the periodic table, for a given ligand and oxidation state of the metal, Δ_o increases going down in a group. e.g., Δ_o is greater in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ than in $[\text{Fe}(\text{NH}_3)_6]^{3+}$.
- $\Delta_t = \frac{4}{9} \Delta_o$.

□ Calculation of CFSE

$$\text{CFSE} = (-0.4x + 0.6y) \Delta_o$$

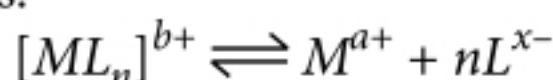
where,

x = number of electrons occupying t_{2g} orbitals.

y = number of electrons occupying e_g orbitals.

□ Stability of Coordination Compounds in Solutions

Consider the following equilibrium between undissociated complex ion and dissociated ions.



$$\text{The equilibrium constant, } K_c = \frac{[\text{M}^{a+}][\text{L}^{x-}]^n}{[(\text{ML}_n)]^{b+}}$$

The smaller the value of K_c , the greater is the stability of complex ion and vice versa. The reciprocal of equilibrium constant is called *stability constant* or K_s .

$$K_s = \frac{1}{K_c} = \frac{[(\text{ML}_n)]^{b+}}{[\text{M}^{a+}][\text{L}^{x-}]^n}$$

The higher the value of K_s , the more is the stability of complex ion. The value of K_s depends on :

- *Nature of central metal atom* : The more the polarizing power of the central metal ion the more is the stability of complex ion.

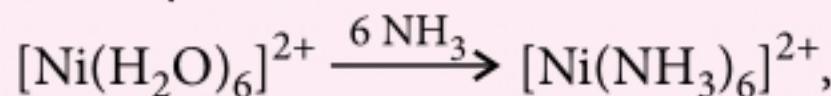
The polarising power $\phi = \frac{\text{charge}}{\text{radius}}$

Thus, complex of Fe^{3+} is more stable than Fe^{2+} .

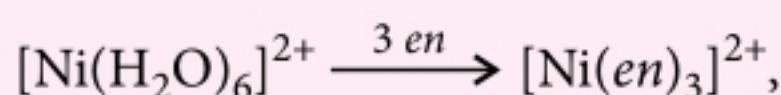
- *Nature of ligand* : Since ligand is a Lewis base, the more the basic character of ligand the more is the stability of complex ion. Thus, complex ion of F^- is more stable than that of Cl^- or Br^- .

KEY POINT

- Chelating ligands give much larger values of stability constant.



$$K_f = 4 \times 10^8$$



$$K_f = 2 \times 10^{18}$$

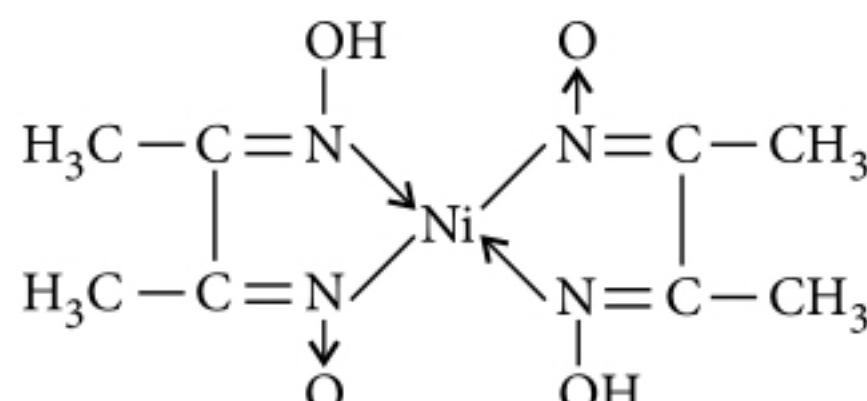
- For complexes in a ligand field, *d*-orbital occupancy depends on Δ_o and pairing energy, P .
 - If $\Delta_o > P$ (strong field ligand), electron pair-up in lower energy *d*-subshell first and forms low spin complex.
 - If $\Delta_o < P$ (weak field ligand), electrons spread out among all *d*-orbitals before pairing up and forms high spin complex.

Importance of Coordination Compounds

□ Biological Processes

- *Haemoglobin* : Oxygen carrier is a complex of iron (II).
- *Chlorophyll* : Green colouring matter of plants is a complex of Mg.
- *Vitamin B₁₂* : Is a complex of cobalt.

□ Analytical chemistry : Many metal ions are quantitatively estimated by complex formation. e.g., Cu^{2+} , Ni^{2+} , Al^{3+} .

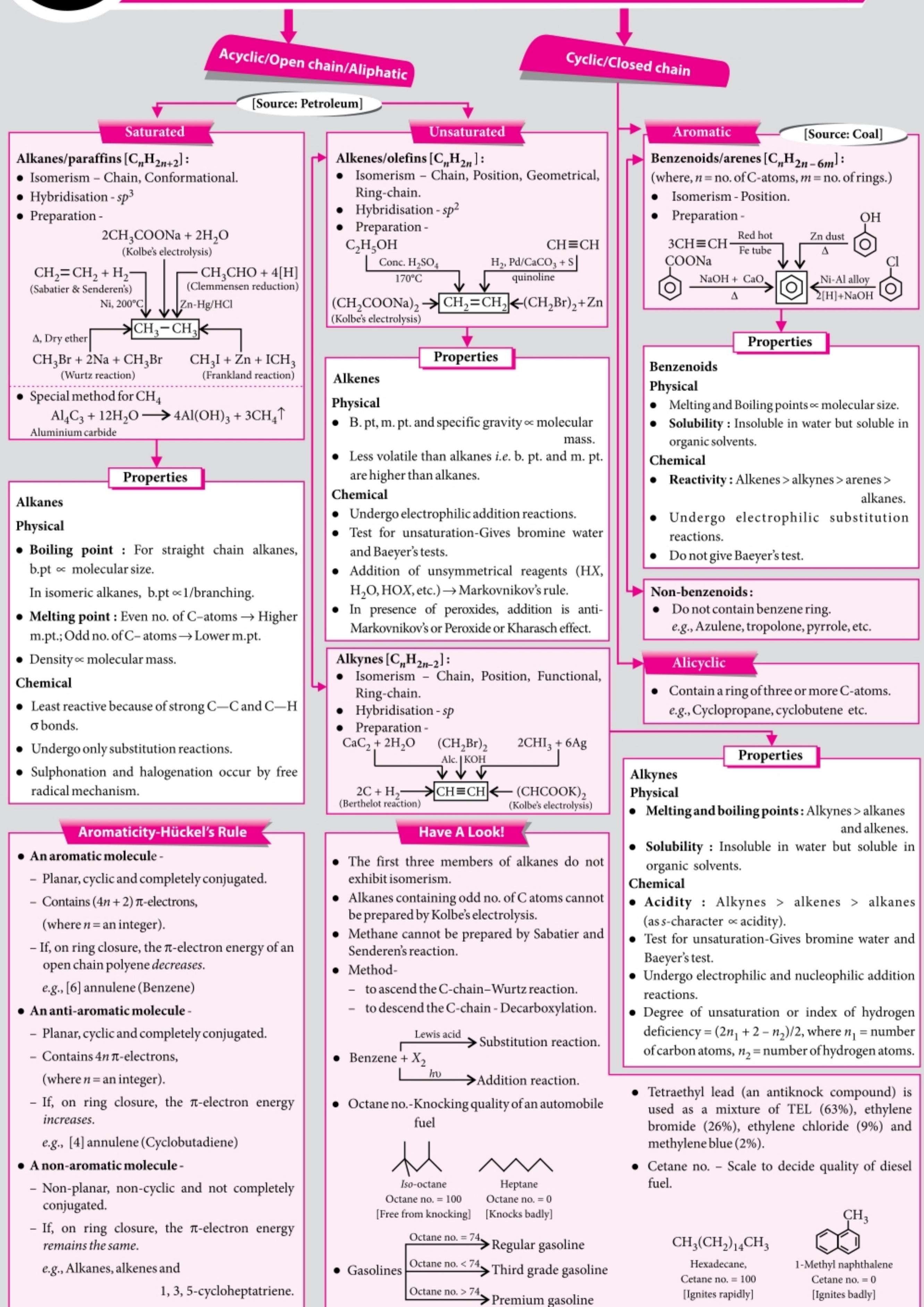


Red precipitate of nickel with dimethyl glyoxime

**CONCEPT
MAP**

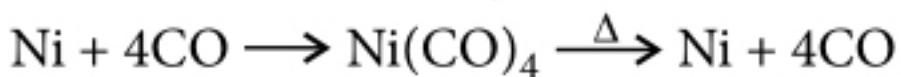
HYDROCARBONS

Compounds composed entirely of carbon and hydrogen atoms bonded to each other by covalent bonds.

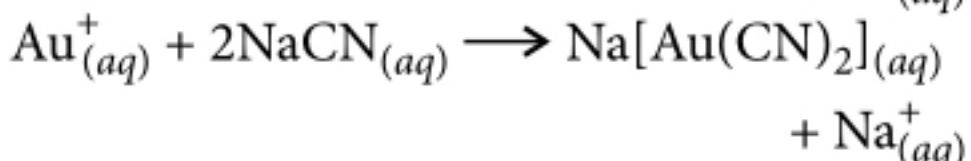
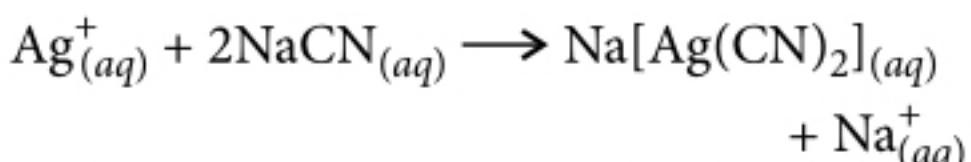


□ Metallurgical Processes

- Nickel is purified by *Mond's process* forming volatile nickel carbonyl.



- Extraction of silver and gold by cyanide process involves complex formation.



ENVIRONMENTAL CHEMISTRY

- Introduction
- Classification of pollutants
- Types of pollution : Air, water and soil pollution

TIPS TO REMEMBER

- **Environmental chemistry** is the branch of chemistry that deals with the study of various chemical processes taking place in the various segments of the environment.
- **Hydrosphere** : Water bodies (sea, oceans, rivers, lakes, etc.) cover about 75% of earth's surface.
- **Lithosphere** : Solid part consisting of soil, rocks, mountains, etc.
- **Biosphere** : Part where living organisms interact with lithosphere, hydrosphere and atmosphere.
- **Abiotic components (non-living)**: Lithosphere, hydrosphere, atmosphere.

□ Tropospheric Pollution

Pollutants	Major sources	Effects
CO	Incomplete combustion of carbonaceous matter in automobile engines and defective furnaces, incomplete combustion of agricultural and slash matter, volcanic eruptions, forest fires.	Carbon monoxide is toxic. It binds with haemoglobin in red blood cells and prevents them from combining with oxygen. Low levels of CO cause headaches and dizziness. Concentrations of ~1% causes death in minutes.
NO _x	Combustion of fuel, natural forest fires, anthro-stationary combustion sources (factories and power plants), transportation.	Toxic to living tissues, harmful to paints, textiles and metals.

- **Biotic components (living)** : Plants, animals, human beings.

- **Medium** : Soil or organism affected by the pollutant or contaminate is called a *receptor*. *Sink* is a chemical medium or species that retains and interacts with the pollutant.

Classification of Pollutants

□ On the Basis of the form in which they Persist

- *Primary pollutants* : Those which remain as such after their formation. e.g., nitric oxide (NO), SO₂, NO₂, CO, hydrocarbons etc.

- *Secondary pollutants* : Formed from the primary pollutants in the atmosphere or hydrosphere. For example, hydrocarbons and oxides of nitrogen react together photochemically to form certain compounds e.g., PANs i.e. peroxyacetyl nitrates.

□ On the Basis of Disposal

- *Degradable pollutant* : Degrades after some time either automatically i.e., by heating or through action of microorganisms (bio-degradable, e.g., sewage).
- *Non-degradable pollutant* : It does not get degraded or broken down into harmless material, e.g., DDT, plastics.

Types of Pollution

- **Air pollution** : It is the addition of undesirable materials into the atmosphere either due to natural phenomena or due to human activity on the earth which adversely affect the quality of the air and hence, affects the life on the earth.

SO_x	Anthro-stationary combustion sources, industry found in metal ores, coal, decay products, volcanoes.	They are respiratory tract irritants, low concentration causes throat and eye irritation, causes breathlessness, affect larynx.
Hydrocarbons	Combustion of fuel in automobiles, refineries, anaerobic bacterial decomposition of organic matter, natural gas.	At concentration greater than 500–1000 ppm, they have carcinogenic effect in lungs. They react with O_2 and NO_x to form photochemical smog which have a strong damaging effect on human being as well as plants.
CFC's	CFC's were used primarily as a refrigerants, in aerosol sprays and in the plastics industry. Freons are stable (lasts for over 80 years), inflammable, and inert (in the lower atmosphere).	React with stratospheric ozone. When CFC's are broken down, chlorine free radicals are produced. These can react with more than 10,000 molecules of ozone. Thus, depleting the ozone layer.
Particulates	Volcanic eruptions, fly ash, smelting and mining operations, smoke from incomplete combustion, dust from crushers and grinders.	Inhalation of metallic particles leads to respiratory disorders like asthma, bronchitis, lung cancer, etc.

Greenhouse Effect and Global Warming

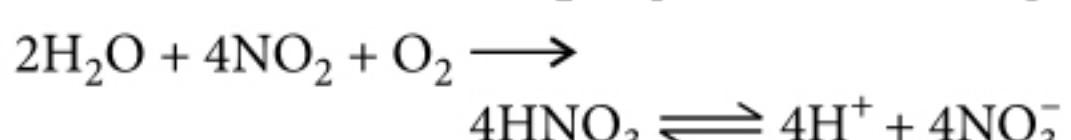
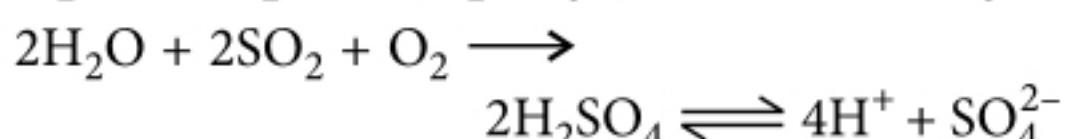
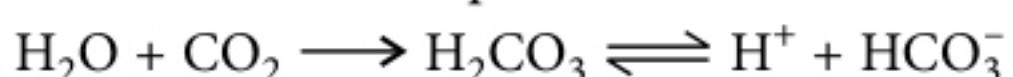
- The retention of heat by the earth and atmosphere from the sun and its prevention to escape into the outer space is known as *greenhouse effect*.
 - Greenhouse gases such as CO_2 , ozone, methane, chlorofluorocarbon compounds and water vapour form a thick cover around the earth which prevents the IR rays emitted by the earth to escape.
 - It gradually leads to increase in temperature of atmosphere.

Consequences of Greenhouse Effect

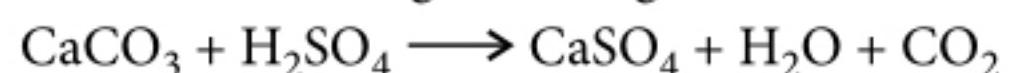
- Global warming would result in rise in sea level due to increased rate of melting of glaciers and floods.
- Spread of some tropical diseases.
- New weather patterns.

Acid Rain

- The oxides of C, N and S present in the atmosphere, dissolve in water and produce acids and lower the pH of water to below 5.6.



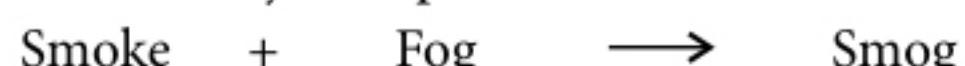
The acids are toxic to vegetation, react with marble and damage buildings.



Acids corrode water pipes and produce salts with heavy metal ions *viz.*, Cu, Pb, Hg and Al toxic in nature.

Smog

- The word *smog* is derived from smoke and fog. It is the major air pollutant.



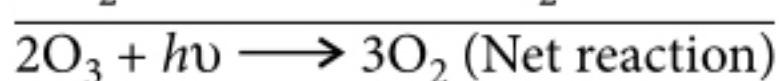
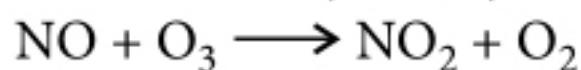
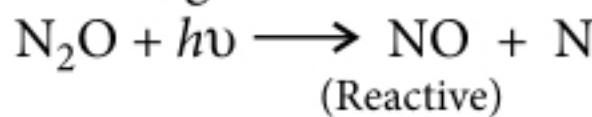
(containing harmful gases)

Classical smog	Photochemical smog
Also called as <i>London smog</i> .	Also called as <i>Los Angeles smog</i> .
Formed due to oxides of sulphur.	Formed due to oxides of nitrogen.
Contains primary pollutants.	Contains secondary pollutants.
Causes bronchitis and problems in lungs.	Causes irritation in eyes.
It is reducing in nature.	It is oxidising in nature.

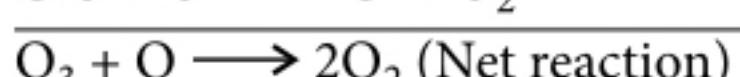
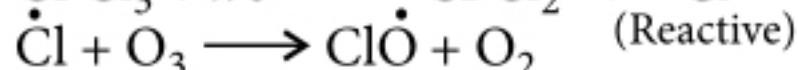
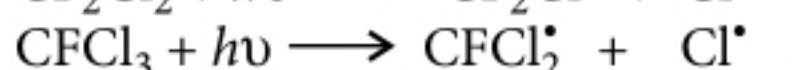
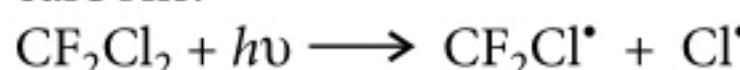
□ Stratospheric Pollution

○ Ozone depletion :

- The ozone layer, existing between 20 to 35 km above the earth's surface, shield the earth from the harmful UV radiations from the sun. The UV radiations cause skin cancer, cataract of eye, and harmful to vegetation.
- Depletion of ozone is caused by oxides of nitrogen.



- The presence of oxides of nitrogen increase the decomposition of O_3 . Depletion of ozone by chlorofluorocarbons.



□ Water Pollution

○ Water pollution is defined as, the contamination of water by foreign substances which makes it harmful for health of animals, plants or aquatic life and makes it unfit for domestic, industrial and agricultural use.

Pollutants	Major sources
Natural wastes	Leaching of minerals, silt from soil erosion, falling of organic matter from banks, etc.
Organic chemicals	Pesticides, surfactants, detergents, industrial wastes.
Metals (Hg, As, Pb, Cd, etc.)	Nuclear power plants, mining, metal plating industries.
Man-made wastes	Sewage, domestic wastes, soaps and detergents, wastes from animal sheds and slaughter houses, run off from agricultural fields, industrial wastes, oil pollution.

○ Effects of water pollution :

- High concentrations of fluoride (over 10 ppm) are poisonous and harmful to bones and teeth.
- Excess nitrate in drinking water can lead to '*blue baby*' syndrome.
- Excess sulphate (> 500 ppm) causes laxative effect.

○ Remedial measures :

- Degradation of organic content of waste water by microbial oxidation.
- Removal of phosphates, coagulation, filtration and disinfection using chlorine for improving the quality of waste water.
- Sewage treatment should be improved.
- Settlement of the filtered waste water to remove suspended solids, oily and greasy material which floats on the surface can be skimmed off.

□ Biochemical Oxygen Demand (BOD) :

It is defined as, the amount of free oxygen required for biological oxidation of the organic matter by aerobic conditions at 20°C for a period of five days. Its unit is mg/L or ppm. An average sewage has BOD value of 100 to 150 mg/L.

□ Chemical Oxygen Demand (COD) :

It is measure of all types of oxidisable impurities (biologically oxidisable and biologically inert organic matter such as cellulose) present in the sewage. COD values are higher than BOD values.

□ Soil Pollution

○ The addition of substances in an indefinite proportion changing the productivity of the soil is known as *soil pollution*.

○ Sources of soil pollution :

- Agricultural pollutants : Chemicals like pesticides, fertilizers, fumigants, insecticides, herbicides, fungicides.
- Domestic refuse and industrial wastes.
- Radioactive wastes from research centres and hospitals.
- Soil conditioners containing toxic metals like Hg, Pb, As, Cd etc.
- Pollutants present in air from chemical works.

○ *Effects of soil pollution :*

- Pollution runs-off into rivers and kills the fishes, plants and other aquatic life.
- Crops and fodder grown on polluted soil may pass on the pollutants to the consumers.
- Soil structure is damaged (clay ionic structure impaired).
- May release vapours and hydrocarbons into buildings and cellars and cause corrosion of foundations and pipelines.
- Contaminated soil decreases soil fertility and hence, there is decrease in the crop yield.
- When soil pollution modifies the soil structure, death of many beneficial soil organisms (e.g. earthworms) in the soil could take place.

- People living near polluted land tend to have higher incidences of migraines, nausea, fatigue, skin disorders and even miscarriages.

○ *Control of soil pollution :*

- Reuse and recycle unwanted items. The less rubbish we create, the less chance the waste will end up in our soil.
- Make use of organic fertilizers and organic pesticides, because they are usually made of natural substances so are biodegradable.
- Insist on buying natural and organic food, because chemical pesticides and fertilizers are not used in their growing process.
- Cut down the usage of paper or use recycled paper.

Exam Café

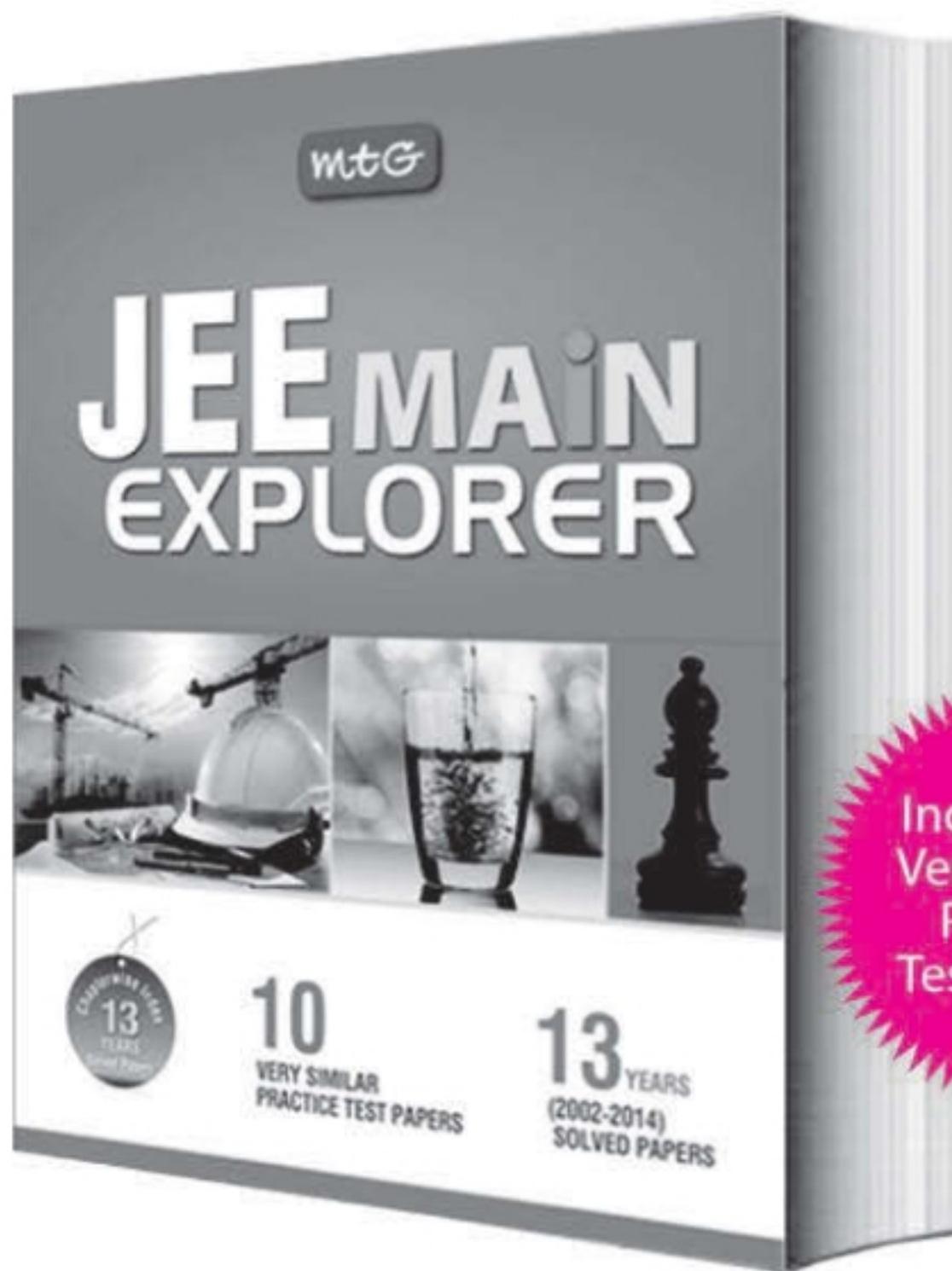
QUESTIONS FOR PRACTICE

1. The IUPAC name of $[\text{Pt}(\text{NH}_3)_4\text{NO}_2\text{Cl}]\text{SO}_4$ is
 - (a) tetraamminechloridonitrito-N-platinum(IV) sulphate
 - (b) tetraamminechloridonitrito-O-platinum(IV) sulphate
 - (c) chloridonitrotetraammineplatinum(IV) sulphate
 - (d) platinum(IV)tetraamminenitrochlorido sulphate.
2. Reagent used to distinguish H_2O_2 and O_3 is
 - (a) lead sulphide
 - (b) starch and iodine
 - (c) potassium permanganate
 - (d) bleaching powder.
3. Which of the following statements is incorrect?
 - (a) All halogens form oxyacids.
 - (b) All halogens show -1 , $+1$, $+3$, $+5$ and $+7$ oxidation states.
 - (c) Hydrofluoric acid forms KHF_2 , K_2F_2 and attacks glass.
 - (d) Oxidising power of halogens follows the order $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

4. Inert atmosphere needed for welding of metals is obtained by
 - (a) Ar, He
 - (b) N_2 , He
 - (c) O_2 , Ne
 - (d) Ar, Ne
5. Native silver metal forms a water soluble complex with a dilute aqueous solution of sodium cyanide in the presence of
 - (a) nitrogen
 - (b) oxygen
 - (c) carbon dioxide
 - (d) argon.
6. The chemical formula for tartar emetic is
 - (a) $\begin{array}{c} \text{CH}(\text{OH})\text{COOH} \\ | \\ \text{CH}(\text{OH})\text{COOK} \end{array}$
 - (b) $\begin{array}{c} \text{CH}(\text{OH})\text{COONa} \\ | \\ \text{CH}(\text{OH})\text{COOK} \end{array}$
 - (c) $\begin{array}{c} \text{CH}(\text{OH})\text{COO}(\text{SbO}) \\ | \\ \text{CH}(\text{OH})\text{COOK} \end{array}$
 - (d) $\begin{array}{c} \text{CH}(\text{OH})\text{COOK} \\ | \\ \text{CH}(\text{OH})\text{COOK} \end{array}$
7. Which of the following statements is incorrect?
 - (a) The average residence time of NO is one month.
 - (b) Limestone acts as a sink for SO_x .

- (c) SO_x can be removed from flue gases by passing through a solution of citrate ions.
 (d) Ammonia acts as a sink for NO_x .
- 8.** Copper sulphate solution decolourises on addition of potassium cyanide due to the formation of
 (a) $[\text{Cu}(\text{CN})_4]^{2-}$ (b) $[\text{Cu}(\text{CN})_4]^{3-}$
 (c) $\text{Cu}(\text{CN})_2$ (d) CuCN
- 9.** The reaction, $3\text{ClO}_{(aq)} \longrightarrow \text{ClO}_{3(aq)}^- + 2\text{Cl}_{(aq)}^-$ is an example of
 (a) oxidation reaction
 (b) reduction reaction
 (c) disproportionation reaction
 (d) decomposition reaction.
- 10.** The molecular shapes of SF_4 , CF_4 and XeF_4 are
 (a) the same with 2, 0 and 1 lone pairs of electrons on the central atoms respectively
 (b) the same with 1, 1 and 1 lone pairs of electrons on the central atoms respectively
 (c) different with 0, 1 and 2 lone pairs of electrons on the central atoms respectively
 (d) different with 1, 0 and 2 lone pairs of electrons on the central atoms respectively.
- 11.** When rain is accompanied by a thunderstorm, the collected rainwater will have a pH value
 (a) slightly lower than that of rainwater without thunderstorm
 (b) slightly higher than that when the thunderstorm is not there
 (c) uninfluenced by the occurrence of thunderstorm
 (d) depends upon the amount of dust in air.
- 12.** A bottle completely filled with conc. H_2SO_4 is left unstoppered for several days and we observe spontaneous overflow of acid. It is due to
 (a) change in temperature
 (b) hygroscopic nature of H_2SO_4
 (c) absorption of air by H_2SO_4
 (d) dehydration of H_2SO_4 .
- 13.** Two compounds pentaamminesulphato-cobalt(III) bromide and pentaamminesulphato-cobalt(III) chloride represent
 (a) linkage isomerism
 (b) ionisation isomerism
- (c) coordination isomerism
 (d) no isomerism.
- 14.** Bordeaux used as a fungicide is a mixture of
 (a) CuSO_4 and $\text{Ca}(\text{OH})_2$
 (b) CaSO_4 and $\text{Cu}(\text{OH})_2$
 (c) CuCO_3 and $\text{Cu}(\text{OH})_2$
 (d) CuO and CaO
- 15.** Select the correct statement(s) regarding the behaviour of HF as a non-aqueous solvent.
 (a) HCl behaves as an acid and HF as a base.
 (b) HClO_4 behaves as a base and HF as an acid.
 (c) HNO_3 and H_2SO_4 behave as base and HF as an acid.
 (d) All are correct.
- 16.** Oxidation of hydrogen halide, HX affords a method for the industrial and laboratory preparation of the halogen, X_2 in the free state in respect of all of the following except
 (a) fluorine (b) chlorine
 (c) bromine (d) iodine.
- 17.** Which of the following molecules has planar structure?
 (a) N_2F_3^+ (b) NH_2OH
 (c) PSCl_3 (d) PF_3Cl_2
- 18.** Which of the following substances are regulated by the Kyoto Protocol?
 I. Argon II. Carbon dioxide
 III. Nitrogen IV. Nitrous oxide
 V. Sulphur hexafluoride
 (a) I, II and III (b) I and III
 (c) II and V (d) II, IV and V
- 19.** In which of the following coordination entities the magnitude of Δ_o (CFSE in octahedral field) will be maximum? (At. no. of Co = 27)
 (a) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ (b) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 (c) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (d) $[\text{Co}(\text{CN})_6]^{3-}$
- 20.** The colour of CuCr_2O_7 solution in water is green because
 (a) $\text{Cr}_2\text{O}_7^{2-}$ ions are green
 (b) Cu^{2+} ions are green
 (c) both $\text{Cr}_2\text{O}_7^{2-}$ and Cu^{2+} ions are green
 (d) Cu^{2+} ions are blue and $\text{Cr}_2\text{O}_7^{2-}$ ions are yellow.

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SOLUTIONS

- 1. (a) :** $[\text{Pt}(\text{NH}_3)_4\text{NO}_2\text{Cl}]\text{SO}_4$
Tetraamminechloridonitrito-N-platinum(IV) sulphate

2. (c) : The pink colour of potassium permanganate is decolourised by H_2O_2 and not by O_3 .

$$\begin{array}{rcl} 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 & \longrightarrow & \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 \\ & & + 3\text{H}_2\text{O} + 5\text{O}_2 \\ [\text{H}_2\text{O}_2 & \longrightarrow & \text{H}_2\text{O} + \text{O}] \times 5 \\ [\text{O} + \text{O} & \longrightarrow & \text{O}_2] \times 5 \end{array}$$

$$2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}_2 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2$$

3. (b) : Fluorine shows only -1 oxidation state.

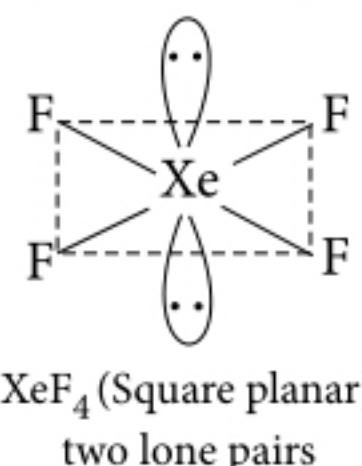
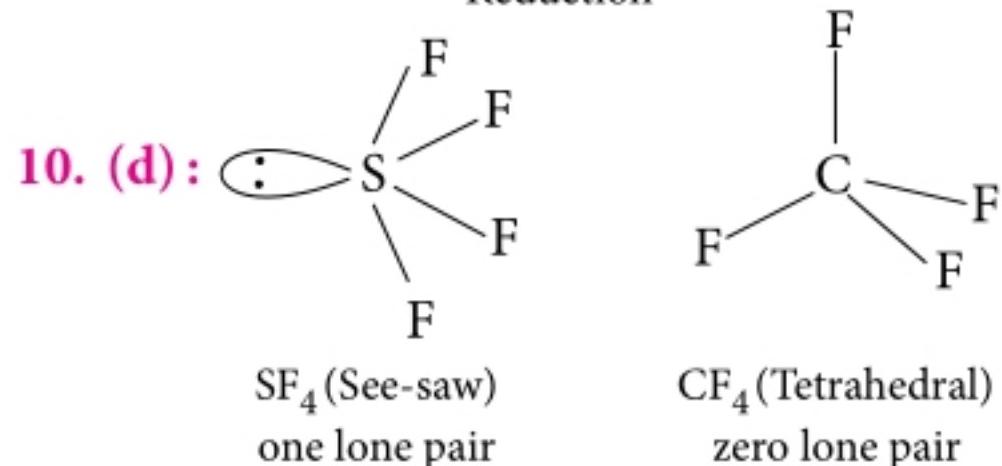
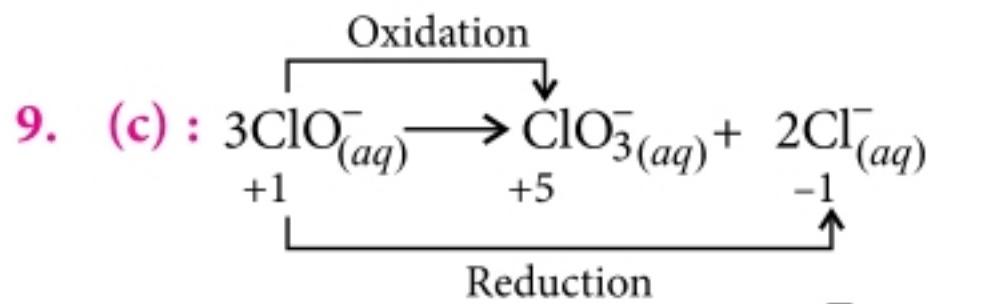
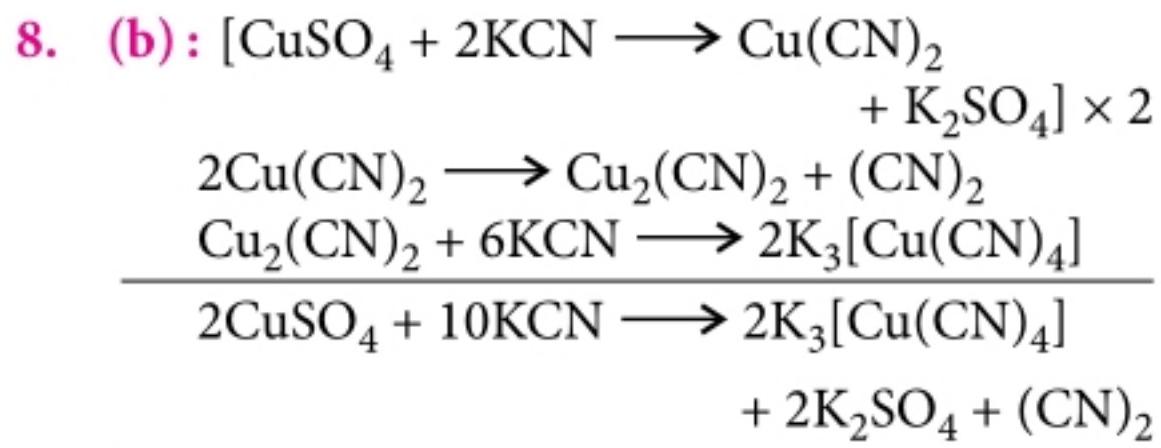
4. (a)

5. (b) : Metallic silver dissolves in sodium cyanide solution in the presence of oxygen to form water soluble complex *i.e.*, sodium argentocyanide.

$$\begin{array}{rcl} 4\text{Ag} + 8\text{NaCN} + 2\text{H}_2\text{O} + \text{O}_{2(\text{air})} & \longrightarrow & 4\text{Na}[\text{Ag}(\text{CN})_2] + 4\text{NaOH} \end{array}$$

6. (c) : Tartar emetic is $\begin{array}{c} \text{CH}(\text{OH})\text{COO}(\text{SbO}) \\ | \\ \text{CH}(\text{OH})\text{COOK} \end{array}$

7. (a) : The average residence time of NO is 4 days.



11. (a) : Normal rainwater has pH 5.6. Thunderstorm results in the formation of NO and HNO_3 which lowers the pH.

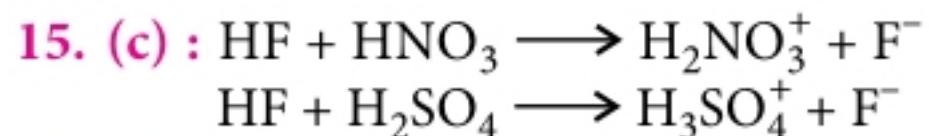
12. (b)

13. (d) : Pentaamminesulphatocobalt(III) bromide : $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$

Pentaamminesulphatocobalt(III) chloride : $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Cl}$

Two compounds have different molecular formulae hence no isomerism exists between the two.

14. (a) : Bordeaux mixture is CuSO_4 and $\text{Ca}(\text{OH})_2$.



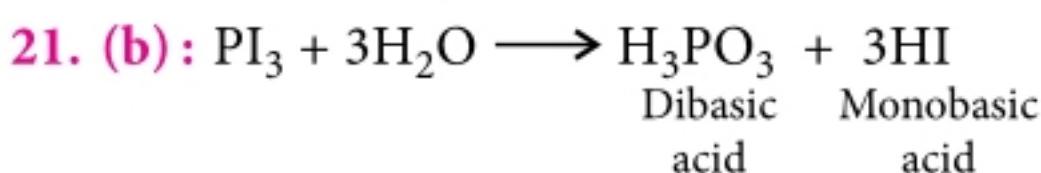
16. (a)

17. (a) : (a) Planar
(b) Pyramidal at N and bent at O
(c) Tetrahedral
(d) Trigonal bipyramidal with apical Cl atom.

18. (d)

19. (d) : Greater the charge on central metal ion and stronger the field of ligand, greater is the Δ_o value (CFSE). According to the spectrochemical series, the increasing order of Δ_o is $\text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NH}_3 < \text{CN}^-$

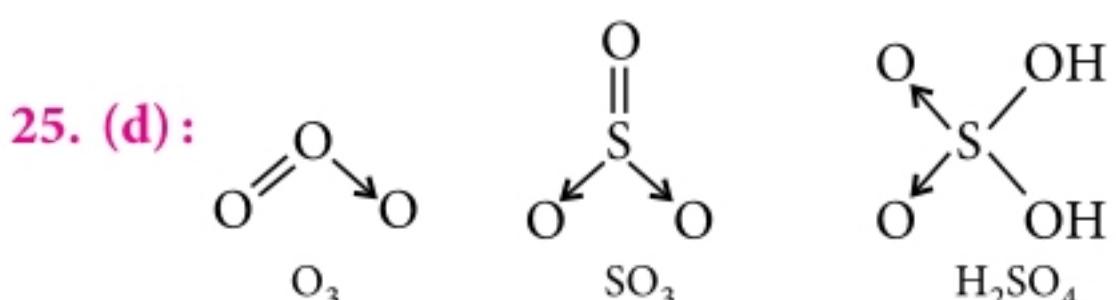
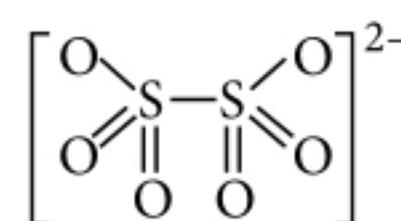
20. (d) : CuCr_2O_7 solution is green because Cu^{2+} ions are blue and $\text{Cr}_2\text{O}_7^{2-}$ ions are yellow in aqueous medium. Both blue and yellow colours mix up to give green colour.



22. (b) : Antichlor is a compound which removes unreacted chlorine from a material. For example hypo.

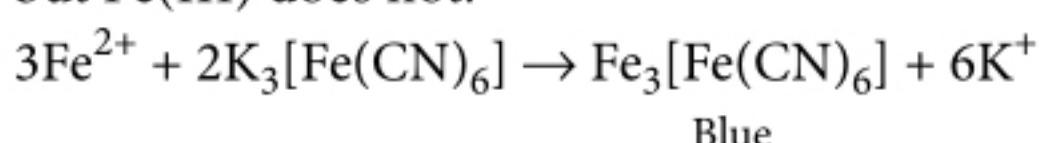
23. (a) : PSCs react with chlorine nitrate and HCl to give HOCl and Cl_2 .

24. (b) : Dithionite ion ($\text{S}_2\text{O}_6^{2-}$) is



26. (c) : If a non-metal is added to the interstitial sites of a metal, then metal becomes even more harder.

27. (b) : Fe(II) gives blue colour with $\text{K}_3[\text{Fe}(\text{CN})_6]$ but Fe(III) does not.



28. (c) : Neon is used in discharge tubes for advertisement purpose.

29. (d) : Metals of group-12 are softer than other transition metals due to comparatively weak metallic bond since their d -electrons do not take part in metallic bonding.

30. (d)



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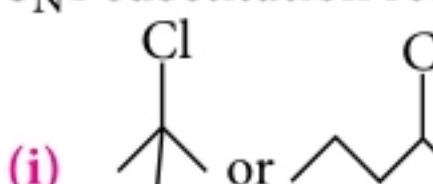
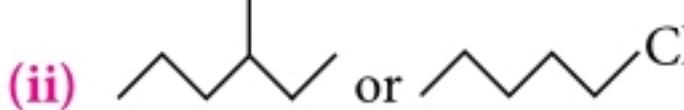
Series- 6 Haloalkanes and Haloarenes | Alcohols, Phenols and Ethers

Time : 3 hrs.

Marks : 70

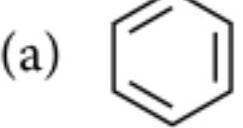
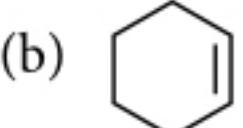
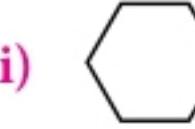
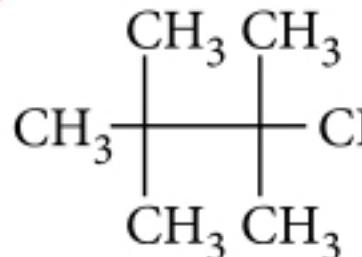
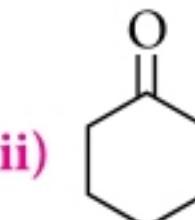
GENERAL INSTRUCTIONS

- (i) All questions are compulsory.
- (ii) Question numbers 1 to 5 are very short-answer questions and carry 1 mark each.
- (iii) Question numbers 6 to 10 are short-answer questions and carry 2 marks each.
- (iv) Question numbers 11 to 22 are also short-answer questions and carry 3 marks each.
- (v) Question number 23 is value based question and carries 4 marks.
- (vi) Question numbers 24 to 26 are long-answer questions and carry 5 marks each.
- (vii) Use Log Tables, if necessary. Use of calculator is not allowed.

1. Why is chloroform stored in brown coloured bottles?
2. Why is ethanol less acidic than water?
3. Why is sulphuric acid not used during the reaction of alcohols with KI?
4. How do you account for the miscibility of ethoxyethane with water?
5. Phenols do not undergo substitution of the $-OH$ group like alcohols, why?
6. What are the products of the following reactions?
(i) $CH_3CH_2CH=CH_2 + HBr \xrightarrow{\text{Peroxide}}$
(ii) $CH_3CH=C(CH_3)_2 + HBr \longrightarrow$
7. Give equations of the following reactions :
(i) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.
(ii) Treating phenol with chloroform in the presence of aqueous $NaOH$ followed by hydrolysis.
8. Write the IUPAC names of
(i) ethylidene chloride
(ii) ethylene dichloride.
9. (i) Convert propan-2-one into tertiary butyl alcohol.
(ii) Arrange H_2O , ROH and $CH \equiv CH$ in the increasing order of acidity.
10. Which one in the following pairs undergoes S_N1 substitution reaction faster and why?
(i) 
(ii) 
11. Write the equations for the reactions of hydrogen iodide with
(i) 1-methoxypropane
(ii) methoxybenzene
(iii) benzyl ethyl ether.
12. How can the following conversions be carried out?
(i) Propene to propan-1-ol
(ii) Benzene to 4-bromonitrobenzene
(iii) Aniline to chlorobenzene

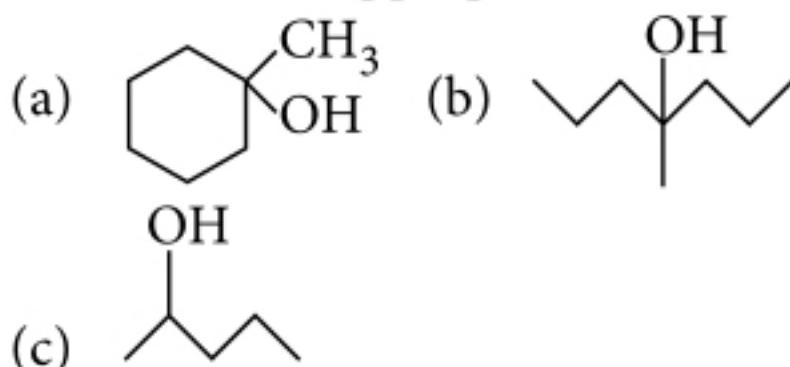
OR

Illustrate with examples the limitations of Williamson's synthesis for the preparation of certain types of ethers.

- 13.** Write the mechanism of hydration of ethene to yield ethanol.
- 14.** Illustrate the following name reactions:
- Wurtz reaction
 - Sandmeyer's reaction
 - Fittig reaction
- 15.** How will you synthesize
- 1-phenylethanol from a suitable alkene
 - cyclohexylmethanol using an alkyl halide by S_N2 reaction.
 - pentan-1-ol using a suitable alkyl halide.
- 16.** (i) Give the IUPAC name and structural formula of D.D.T.
(ii) Complete the following:
-  + $Cl_2 \xrightarrow{U.V. \text{ light}}$
 -  + $Br_2 \xrightarrow[\text{U.V. light}]{\text{Heat}}$
- 17.** Write equations of the following reactions:
- Nitration of anisole
 - Bromination of anisole in ethanoic acid medium
 - Friedel-Crafts acylation of anisole.
- 18.** Arrange the compounds of each set in order of reactivity towards S_N2 displacement:
- 2-Bromo-2-methylbutane,
1-Bromopentane, 2-Bromopentane
 - 1-Bromo-3-methylbutane,
2-Bromo-2-methylbutane,
2-Bromo-3-methylbutane
 - 1-Bromobutane,
1-Bromo-2, 2-dimethylpropane,
1-Bromo-2-methylbutane,
1-Bromo-3-methylbutane
- 19.** (i) Name the reagents and write the chemical equations for the preparation of the following compounds by Williamson's synthesis:
- Ethoxybenzene
 - 2-Methyl-2-methoxypropane
- (ii) Why do phenols not give the protonation reaction readily?
- 20.** What happens when
- n -butyl chloride is treated with alcoholic KOH
- (ii) bromobenzene is treated with Mg in the presence of dry ether
(iii) chlorobenzene is subjected to hydrolysis?
- OR**
- Identify A, B, C, D, E, R and R' in the following:
-  Br + Mg $\xrightarrow{\text{dry ether}}$ A $\xrightarrow{H_2O}$ B
 - $R-Br + Mg \xrightarrow{\text{dry ether}}$ C $\xrightarrow{D_2O}$ CH₃CH(CH₃)_D
 -  $\xleftarrow{Na/\text{ether}}$ R'-X \xrightarrow{Mg} D
 $\downarrow H_2O$ E
- 21.** Write structures of the products of the following reactions:
- $CH_3-CH=CH_2 \xrightarrow{H_2O/H^+}$
 -  $\xrightarrow{NaBH_4}$
 - $CH_3-CH_2-\underset{CH_3}{\overset{|}{C}}-CHO \xrightarrow{NaBH_4}$
- 22.** Explain the following with an example:
- Kolbe's reaction
 - Reimer-Tiemann reaction
 - Williamson's ether synthesis
- 23.** Raj's father wanted to go to the hospital to see his ailing friend. Raj insisted to accompany his father. On reaching the hospital, Raj noticed a peculiar smell.
After reading the passage, answer the following questions:
- Name the chemical compound which causes the hospital smell.
 - What is the use of this chemical and how does it work?
 - How is this chemical prepared in the laboratory?
 - Can we use some other chemical which has the desired effect but no smell?
- 24.** (i) Give chemical tests to distinguish between compounds in each of the following pairs:

- (a) Phenol and Benzyl alcohol
 (b) Butan-2-ol and 2-Methylpropan-2-ol

(ii) How would you synthesize the following alcohols from appropriate alkenes?



OR

(i) How would you account for the following:

- (a) Phenols are much more acidic than alcohols.
 (b) The boiling points of ethers are much lower than those of the alcohols of comparable molar masses?

(ii) Give reason for the following:

- (a) *m*-Aminophenol is stronger acid than *o*-aminophenol.
 (b) Alcohols act as weak base.
 (c) Propanol has higher boiling point than that of the hydrocarbon butane.

25. (i) Primary alkyl halide (A) C_4H_9Br reacted with alcoholic KOH to give compound (B). Compound (B) is reacted with HBr to give (C) which is an isomer of (A). When (A) is reacted with sodium metal it gives compound (D), C_8H_{18} which is different from the compound formed when *n*-butyl bromide was reacted with sodium. Give the structural formula of (A) and write the equations for all the reactions.

(ii) Write the isomers of the compound having molecular formula C_4H_9Br .

OR

(i) Explain why:

- (a) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
 (b) alkyl halides, though polar, are immiscible with water.
 (c) Grignard reagents should be prepared under anhydrous conditions.

(ii) A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single

monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

26. (i) How would you account for the following:

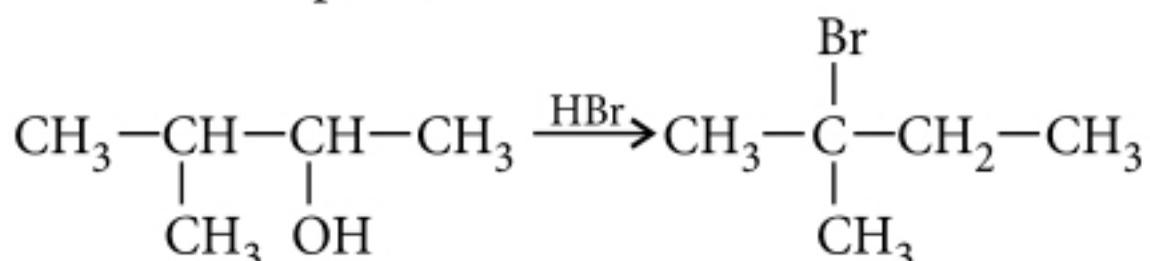
- (a) Ethers possess a dipole moment even if the alkyl radicals in the molecule are identical.
 (b) *o*-Nitrophenol is more acidic than *o*-methoxyphenol.
 (c) Primary alcohols are more acidic than secondary alcohols?

(ii) How are the following conversions carried out?

- (a) Ethyl magnesium chloride to Propan-1-ol
 (b) Methyl magnesium bromide to 2-Methylpropan-2-ol

OR

(i) (a) When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place.

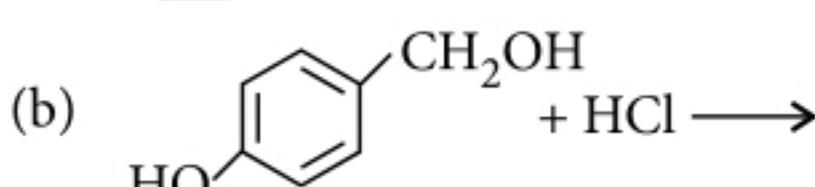
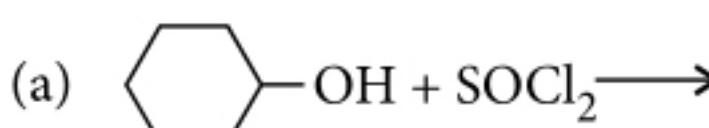


Give a mechanism for this reaction.

(b) How are the following conversions carried out?

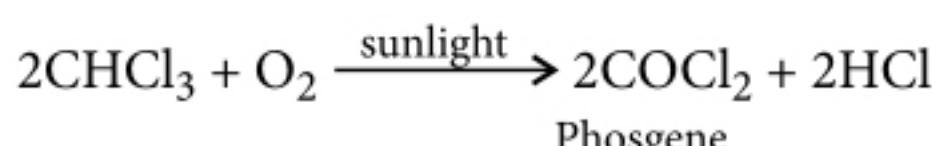
- (i) Ethanol to Propan-2-ol
 (ii) Ethanol to 1,1-Dichloroethane

(ii) Complete the following reaction equations:



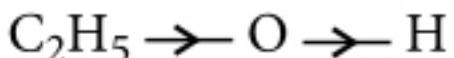
SOLUTIONS

1. In the presence of sunlight and air, chloroform is slowly oxidised to highly poisonous phosgene gas.

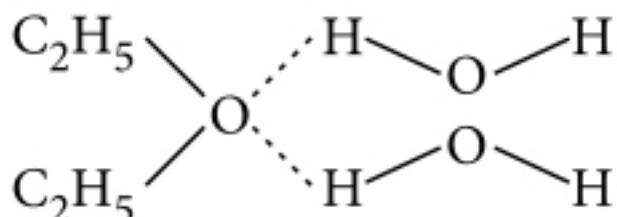


2. The ethyl group in ethanol is electron donating (*+I*-effect) and increases the electron density in

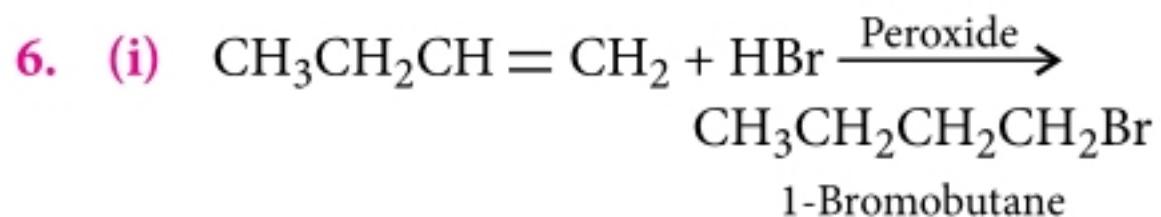
the O — H bond making it difficult to remove H as H^+ ion.



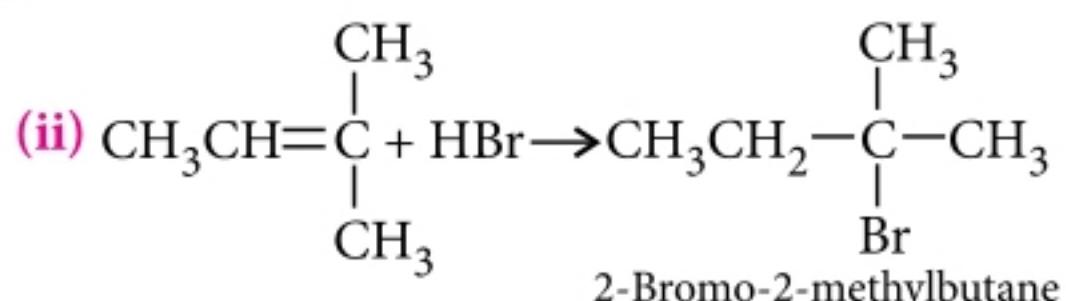
3. H_2SO_4 is a strong oxidising agent and hence oxidises HI produced during the reaction to I_2 .
4. Ethoxyethane is miscible in water because of hydrogen bonding.



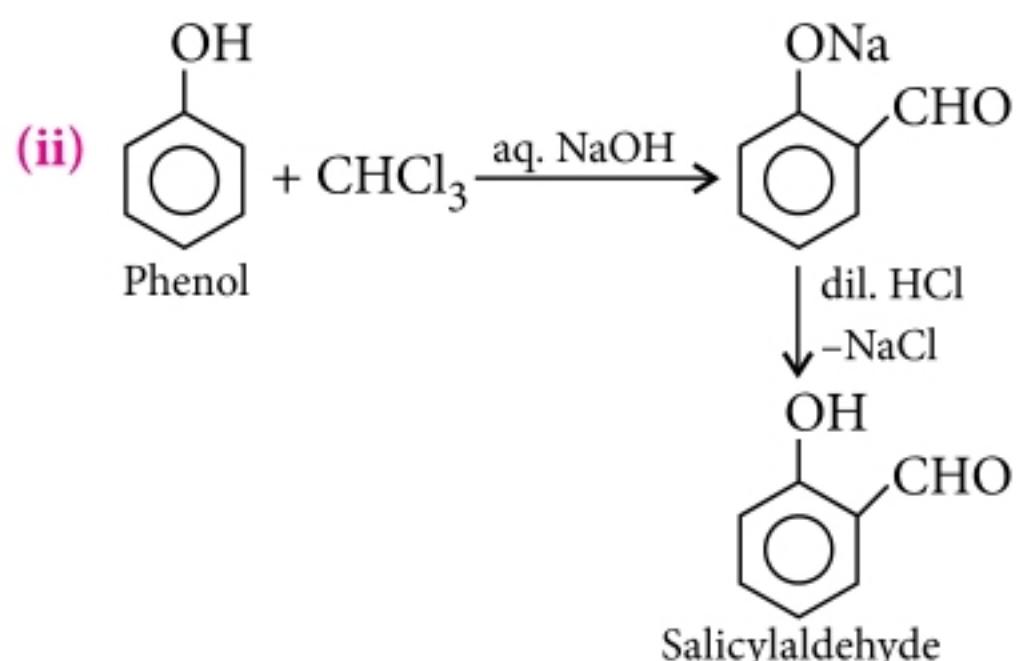
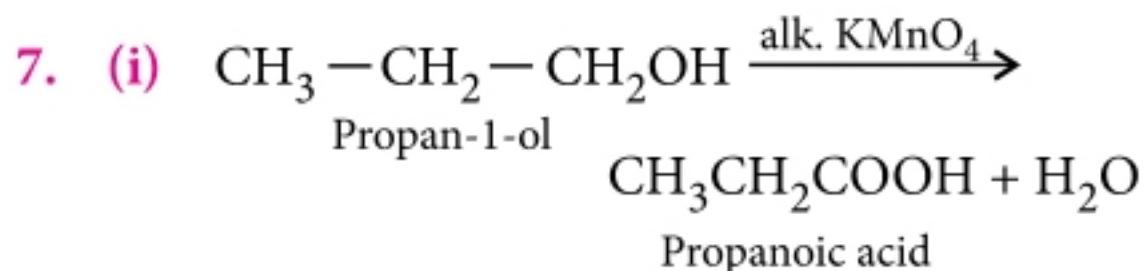
5. The C—Obond in phenols has some double bond character due to resonance and hence cannot be easily cleaved by nucleophile.



Anti-Markownikoff's rule (Kharasch or peroxide effect)

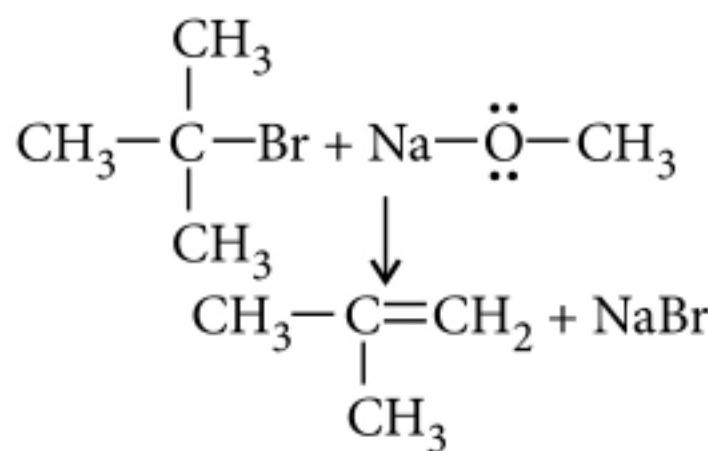


Markownikoff's rule



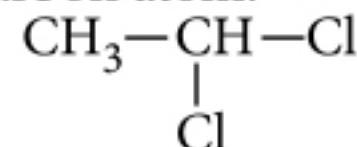
OR

Williamson's synthesis cannot be employed for tertiary alkyl halides as they yield alkenes instead of ethers. The reaction of CH_3ONa with $(\text{CH}_3)_3\text{CBr}$ gives exclusively 2-methylpropene.



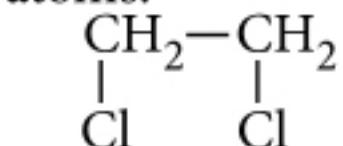
Aryl halides and vinyl halides cannot be used as substrates because of their low reactivity in nucleophilic substitution.

8. (i) Ethyldene chloride is *gem*-dichloride in which both Cl-atoms are attached to the same carbon atom.

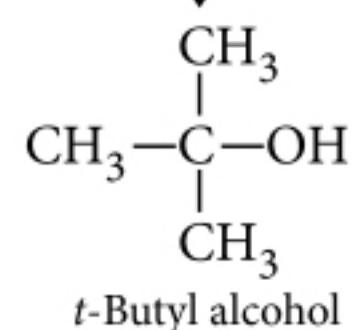
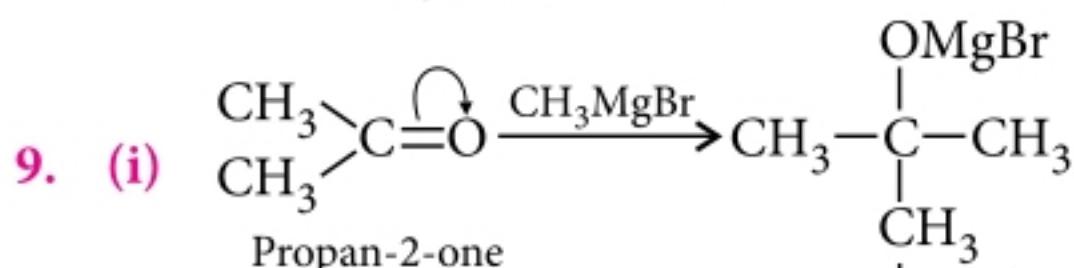


1, 1-Dichloroethane

- (ii) Ethylene dichloride is *vic*-dihalide in which Cl-atoms are attached to adjacent carbon atoms.



1, 2-Dichloroethane



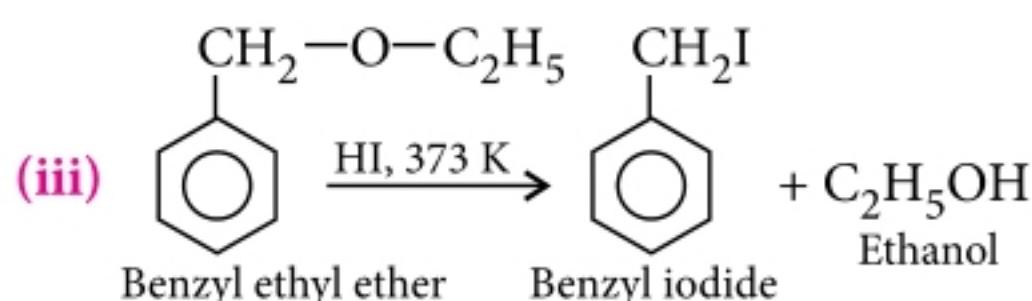
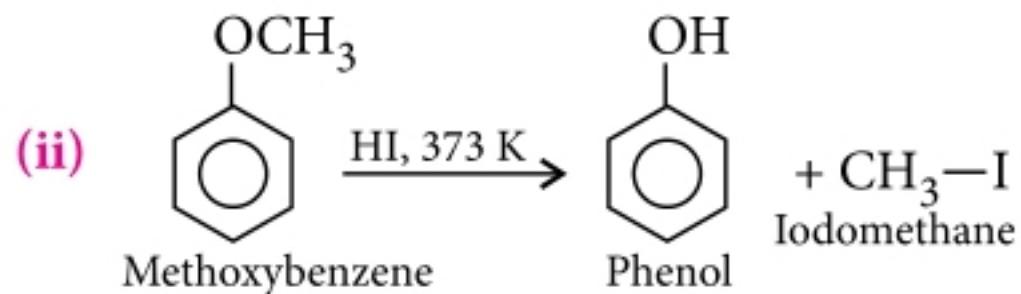
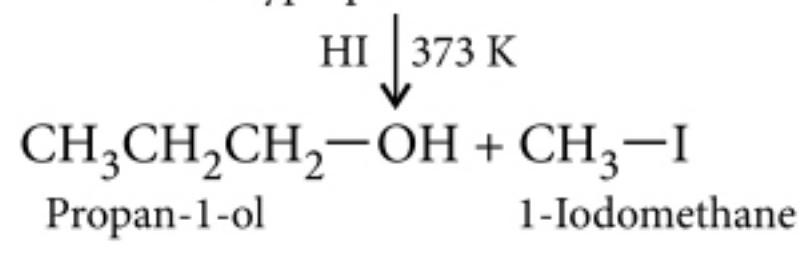
t-Butyl alcohol



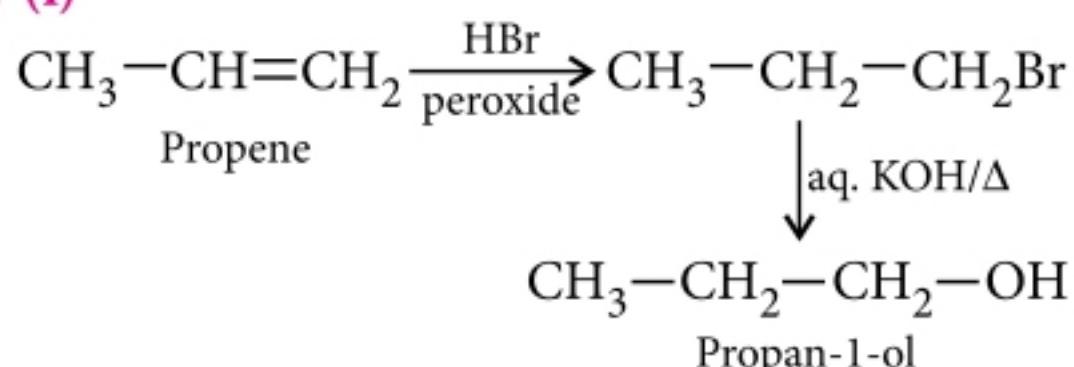
Oxygen is more electronegative than *sp* hybrid carbon and further alkyl group in alcohols increases electron density due to *+I* effect hence, ionisation decreases.

10. (i)
- Tertiary halide reacts faster than secondary halide in $\text{S}_{\text{N}}1$ reaction because of the greater stability of tertiary carbocation intermediate.
- (ii)

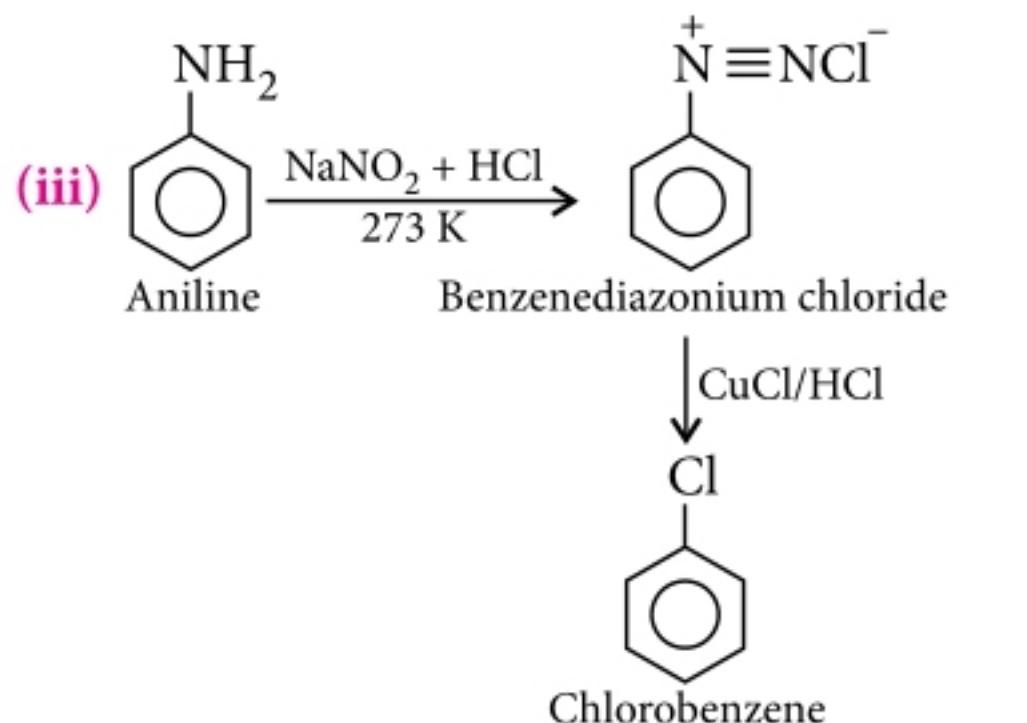
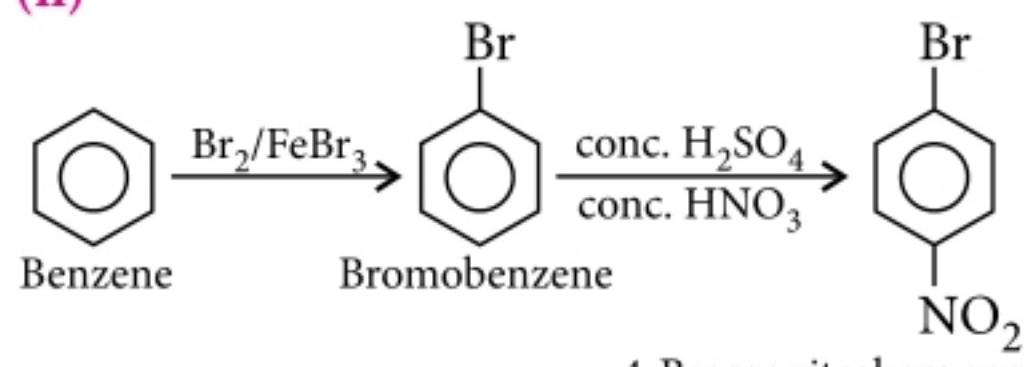
Secondary halide reacts faster because of greater stability of secondary carbocation than primary.
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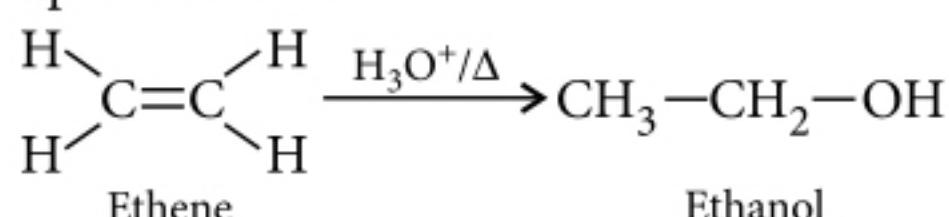
12. (i)



(ii)



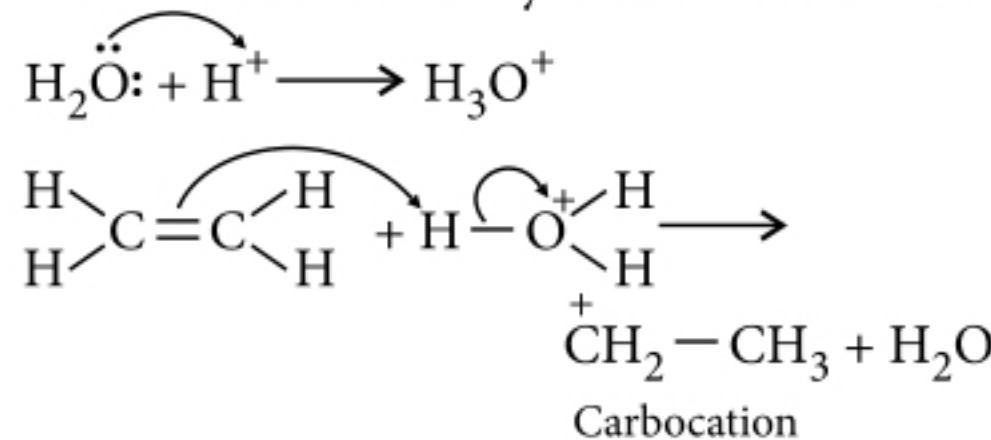
13. The acid catalysed hydration of ethene may be represented as:



The mechanism followed by the above reaction may be depicted as:

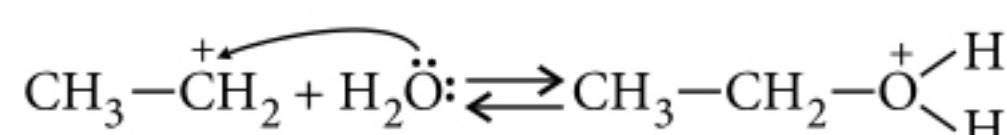
Step 1 : Generation of carbocation :

Protonation of ethene yields a carbocation.



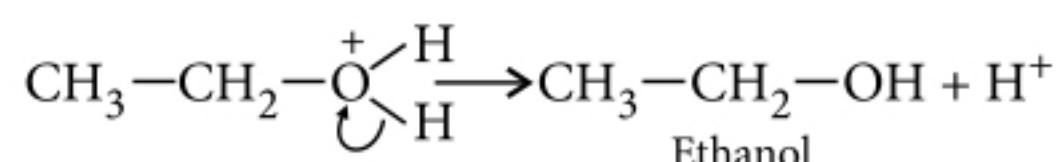
Step 2 : Nucleophilic attack of water on carbocation:

The carbocation polarizes the lone pair of electrons of O of water and hydration takes place.

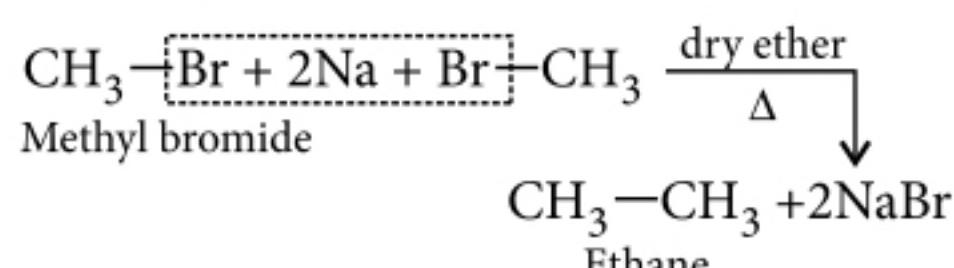


Step 3 : Formation of product :

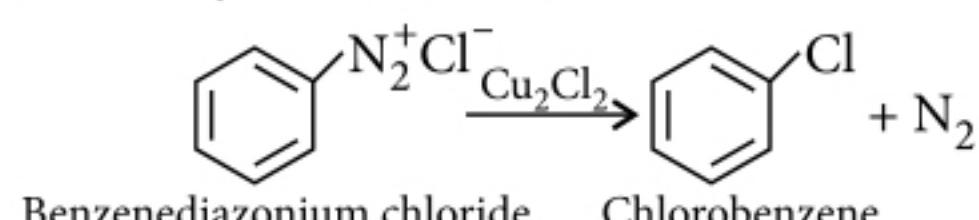
Regeneration of the proton takes place.



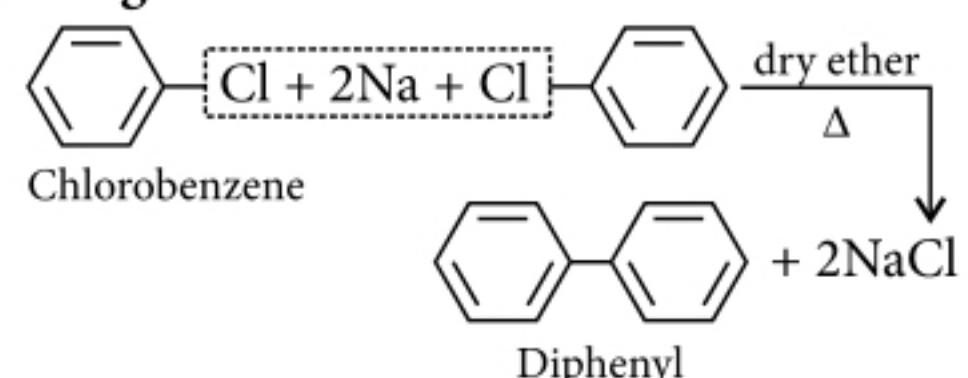
14. (i) Wurtz reaction:



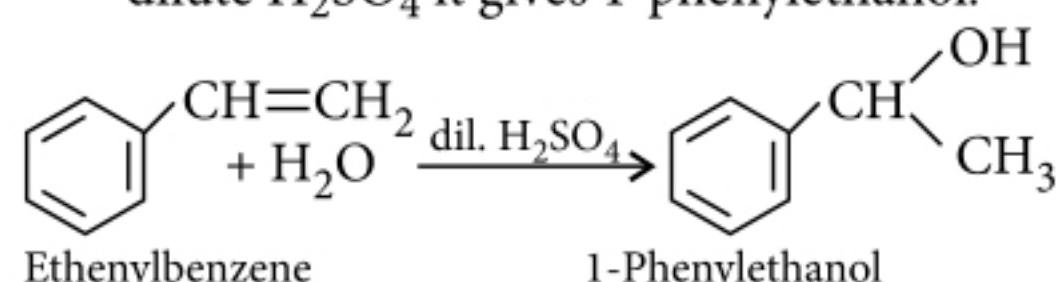
(ii) Sandmeyer's reaction :



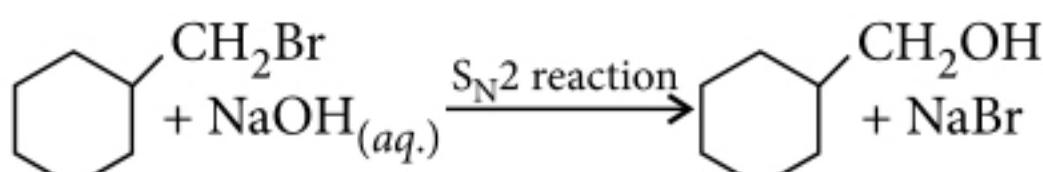
(iii) Fittig reaction:



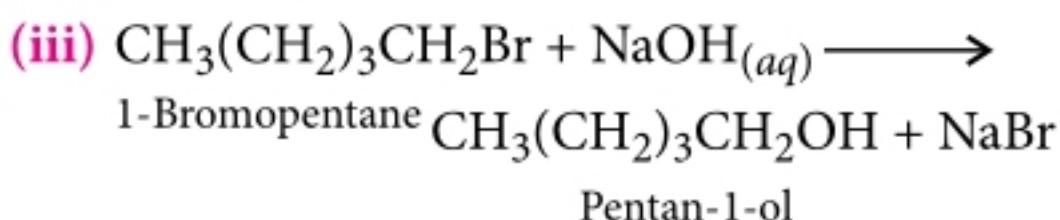
15. (i) When ethenylbenzene is treated with dilute H_2SO_4 it gives 1-phenylethanol.



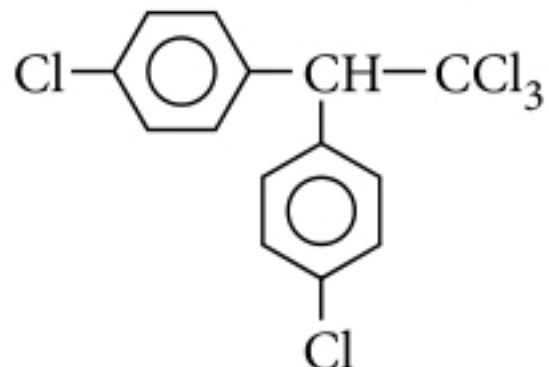
(ii) When cyclohexylmethyl bromide is treated with aq. NaOH , it gives cyclohexylmethanol.



Cyclohexylmethyl bromide Cyclohexylmethanol

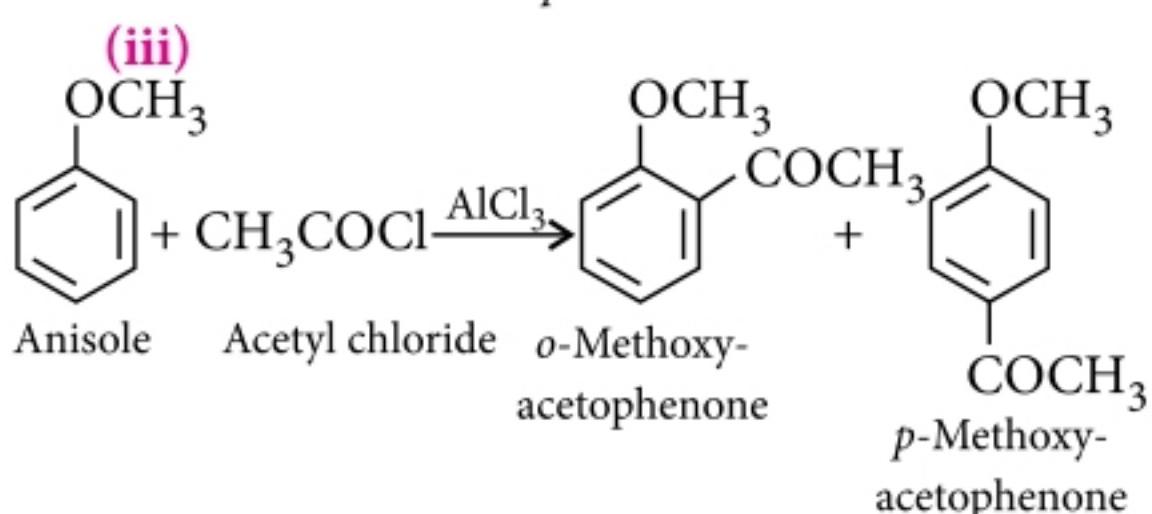
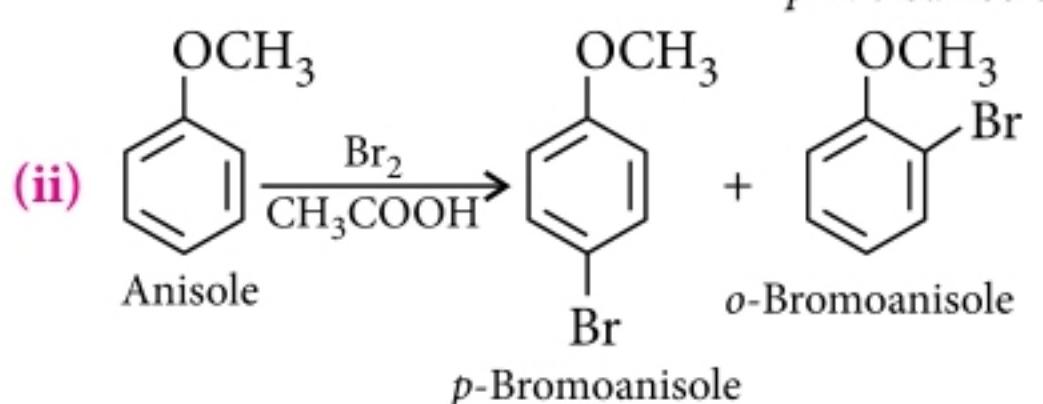
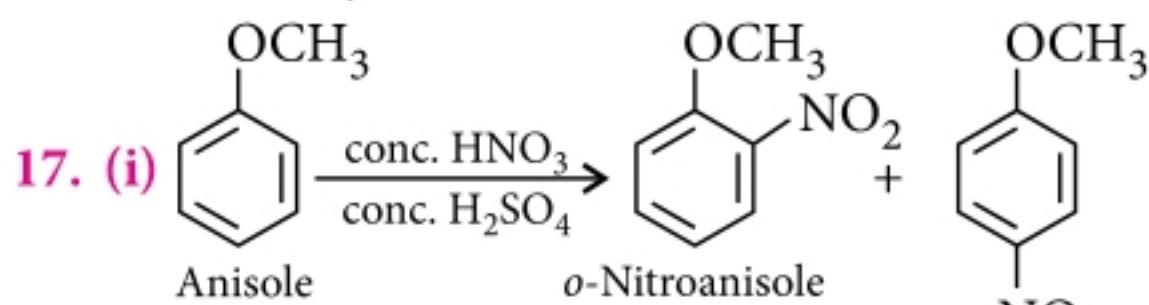
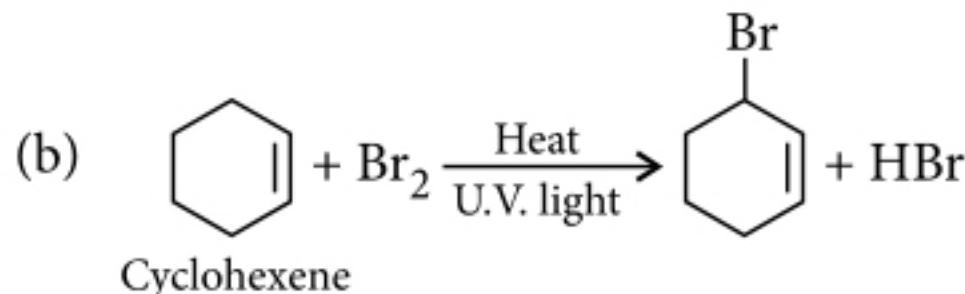
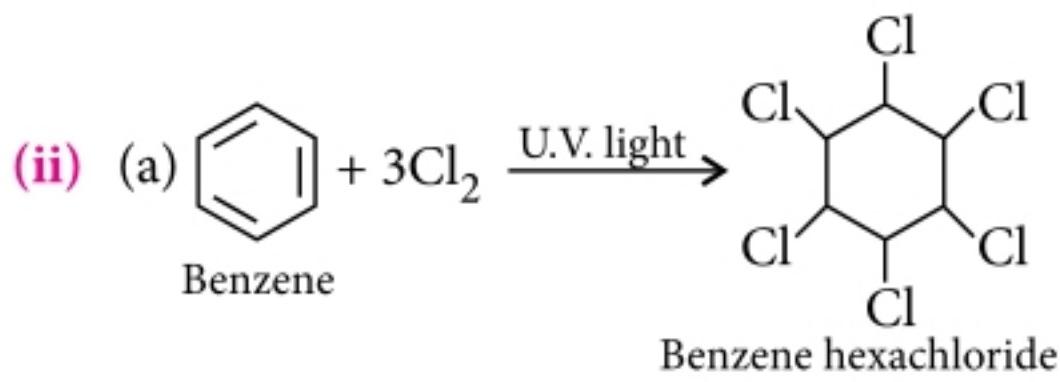


16. (i) D.D.T. (*p,p'*-dichlorodiphenyltrichloroethane)



IUPAC name:

2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane.

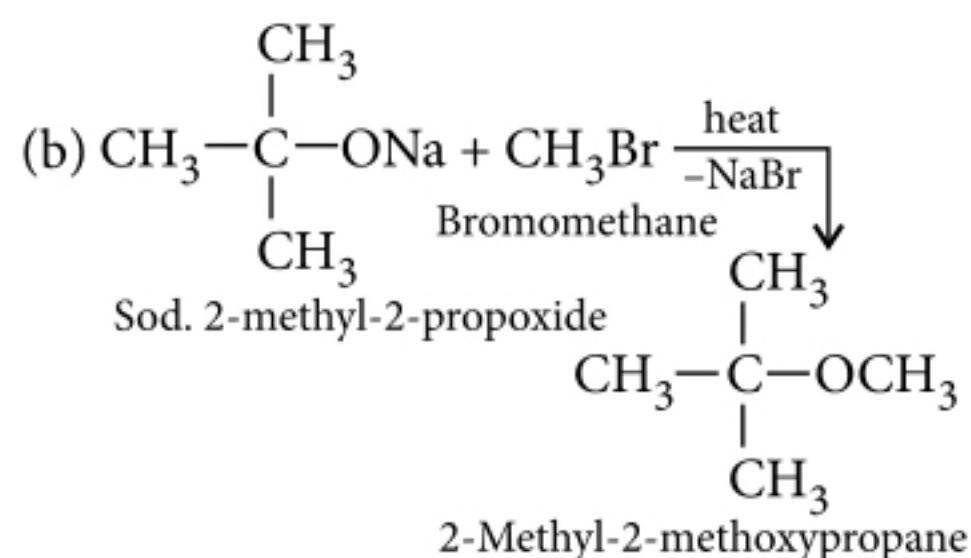
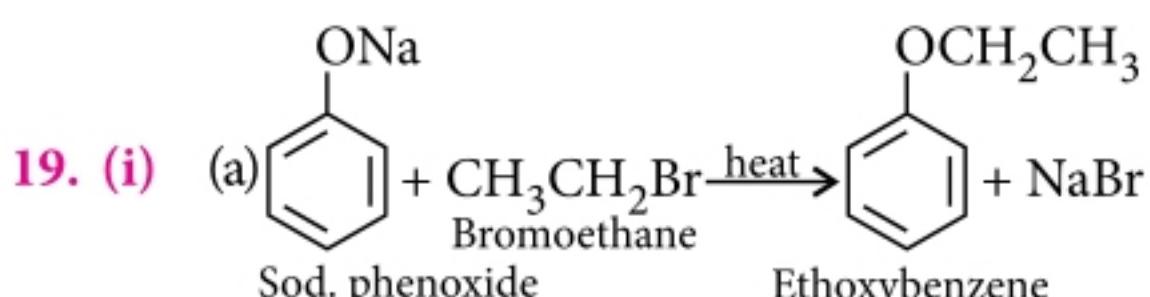


18. The reactivity of alkyl halides towards S_N2 displacement follows the order $3^\circ < 2^\circ < 1^\circ$. This is because primary alkyl halide has lowest steric hinderance and tertiary alkyl halide has highest steric hinderance.

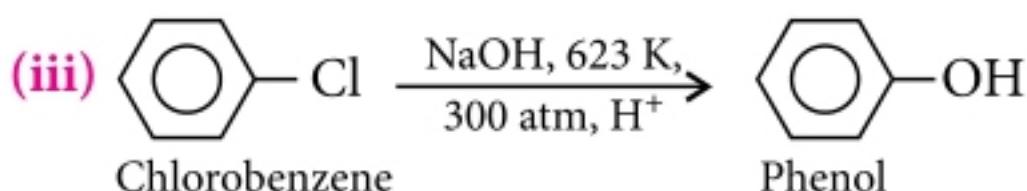
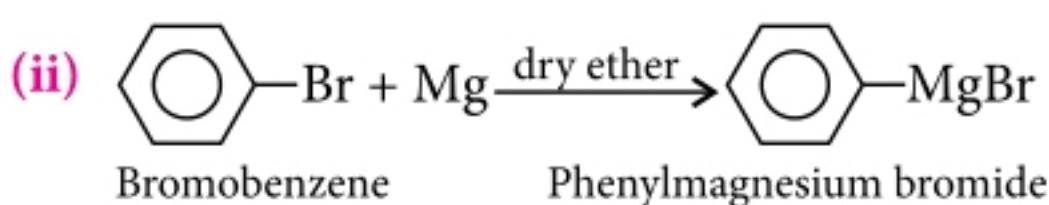
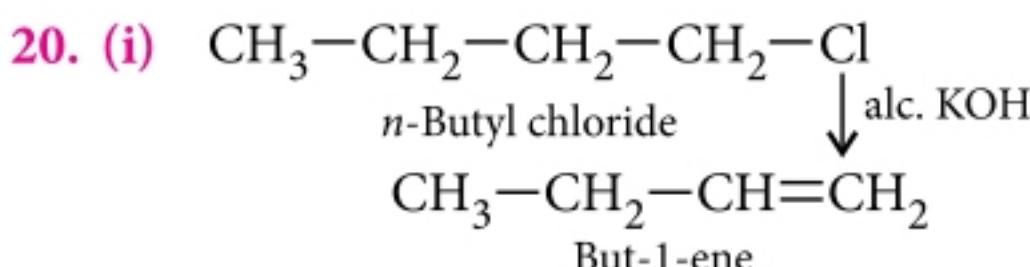
(i) 2-Bromo-2-methylbutane
 $< 2\text{-Bromopentane} < 1\text{-Bromopentane}$

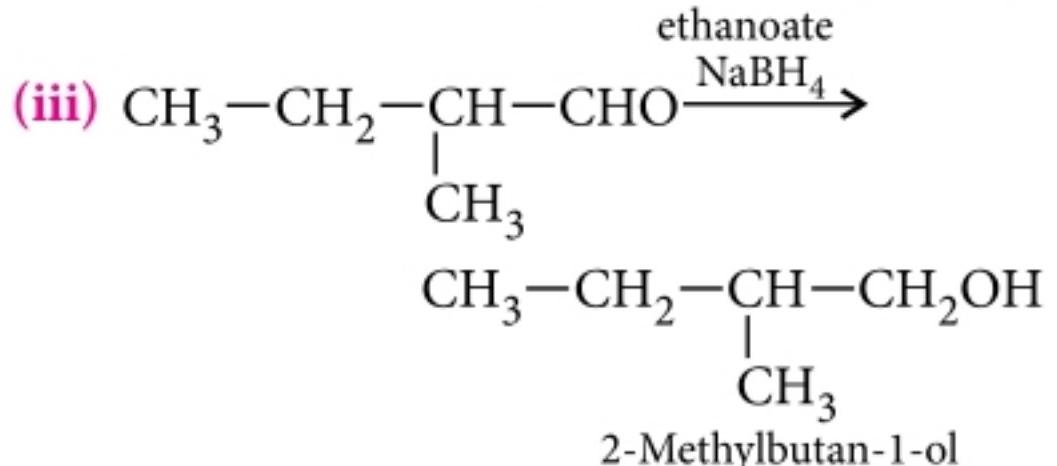
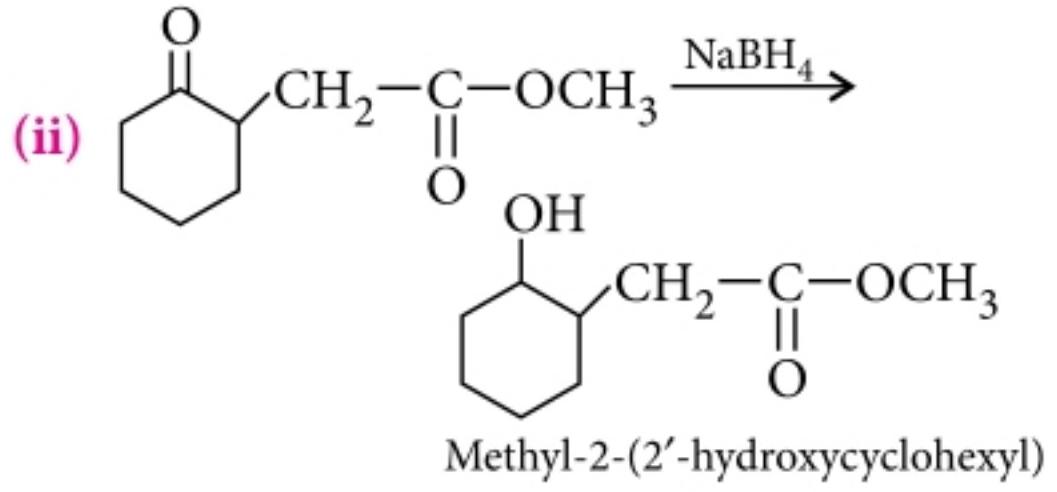
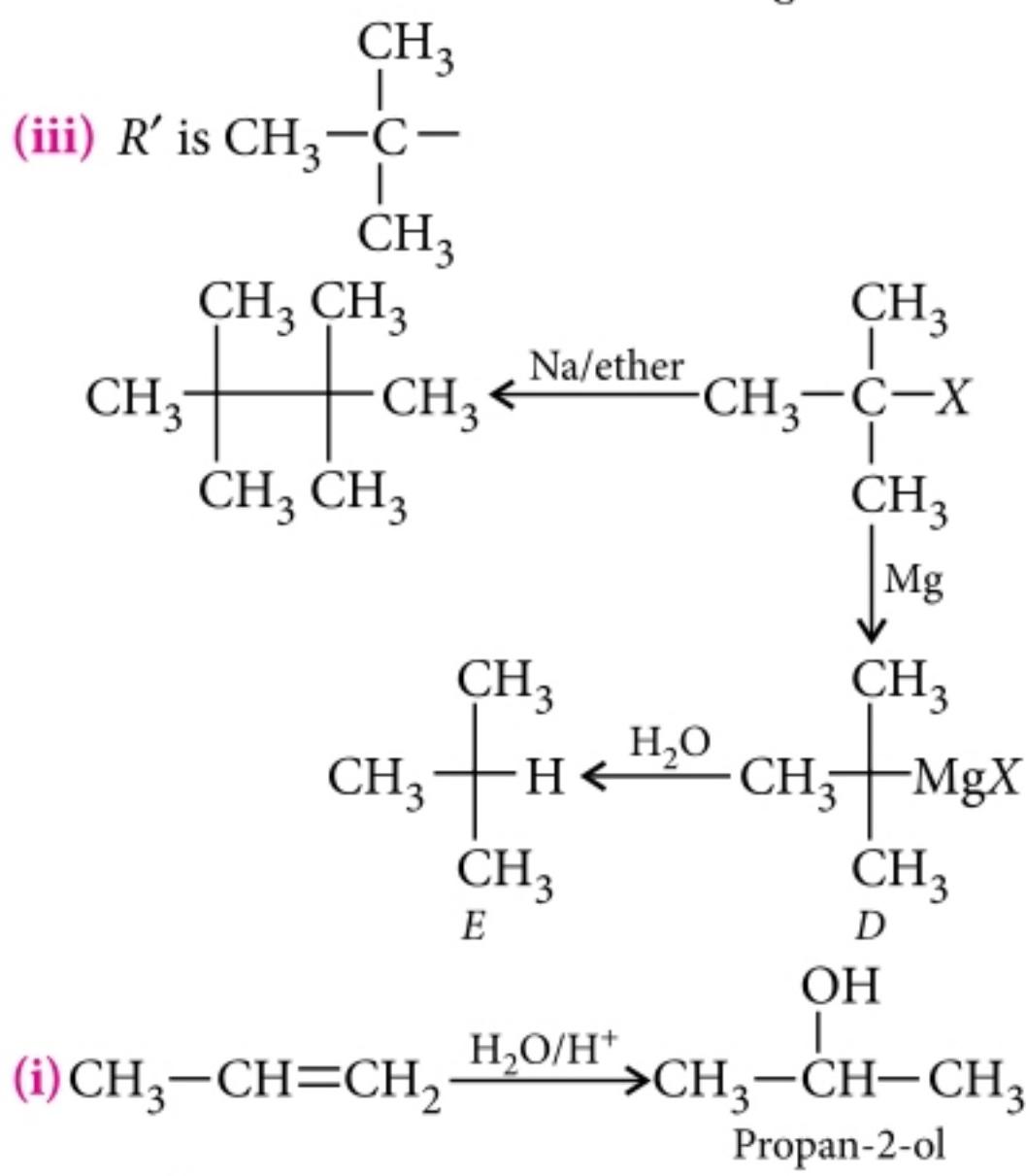
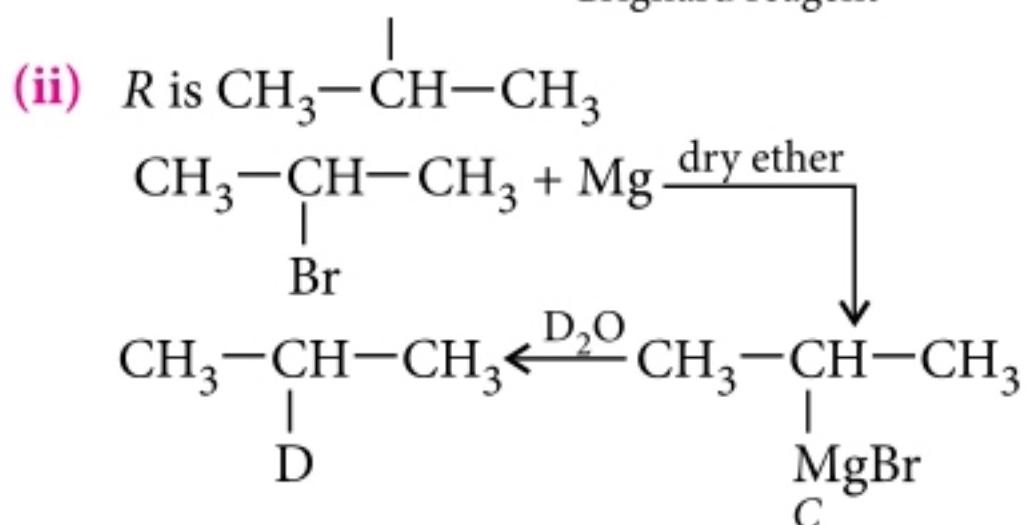
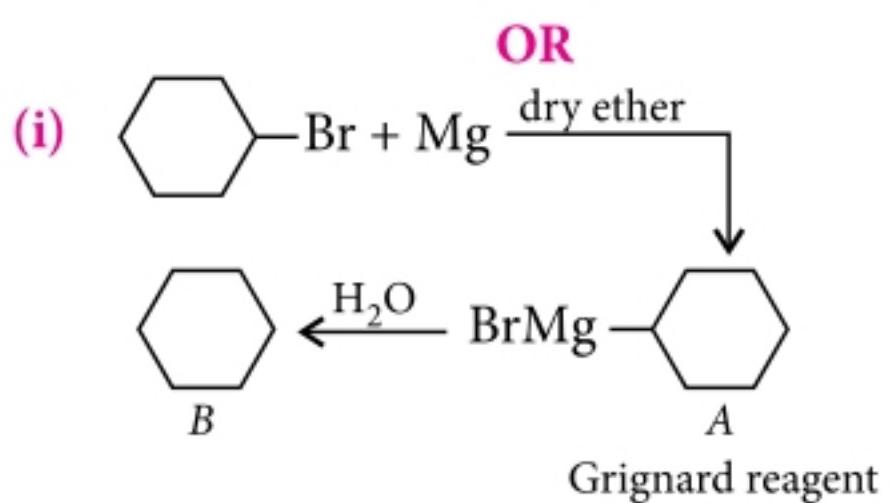
(ii) 2-Bromo-2-methylbutane
 $< 2\text{-Bromo-3-methylbutane} < 1\text{-Bromo-3-methylbutane}$

(iii) 1-Bromo-2, 2-dimethylpropane
 $< 1\text{-Bromo-2-methylbutane} < 1\text{-Bromo-3-methylbutane} < 1\text{-Bromobutane}$
 All these are primary alkyl halides but 1-bromobutane has least steric hinderance and 1-bromo-2, 2-dimethylpropane has most steric hinderance.

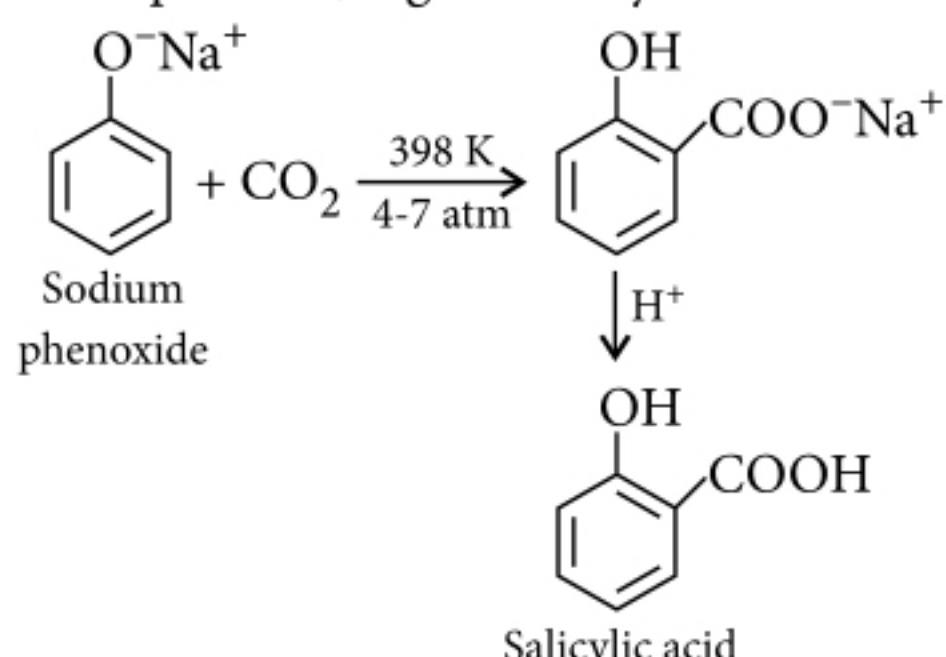


(ii) In phenols, the lone pairs of electrons on the oxygen atom are delocalised over the benzene ring due to resonance and hence are not easily available for protonation.

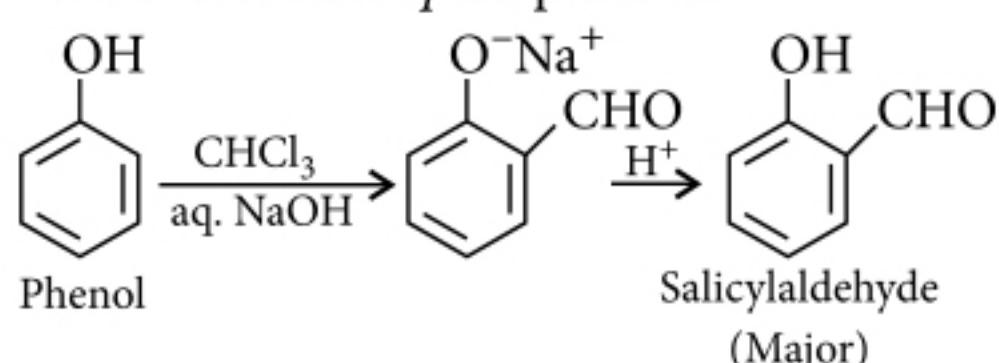




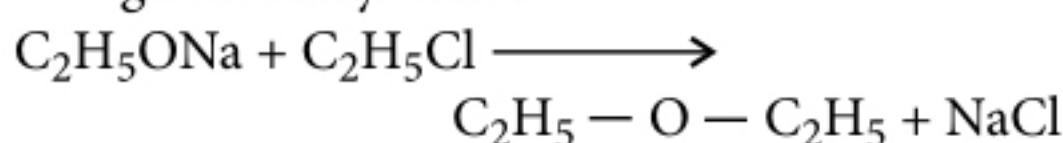
22. (i) Kolbe's reaction : When sodium phenoxide is heated with carbon dioxide under pressure, it gives salicylic acid.



(ii) **Reimer—Tiemann reaction:** This involves the treatment of phenol with chloroform in aqueous sodium hydroxide solution followed by acid hydrolysis. Salicylaldehyde is obtained as the major product along with small amount of *para* product.



(iii) Williamson's ether synthesis : Alkyl halide when treated with sodium alkoxide gives dialkyl ether.



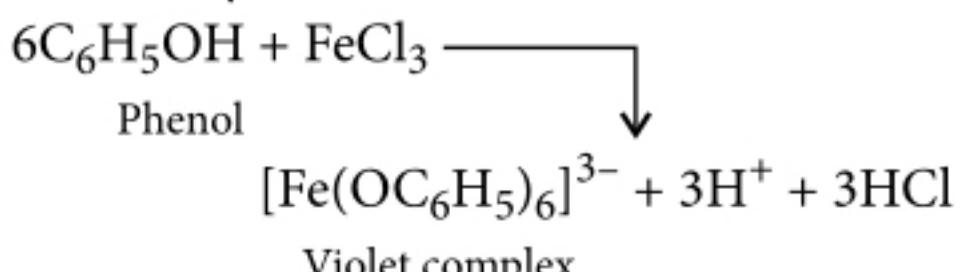
23. (i) It is the smell of a chemical compound called iodoform (CHI_3).

(ii) It is a mild disinfectant and is used for cleaning the floors. It can also be used as an antiseptic for skin infections, burns, etc. When applied on skin, decomposes to release iodine. It is iodine which acts as the actual antiseptic, killing bacteria and fungi. It is also safer than other antiseptics if it is accidentally swallowed.

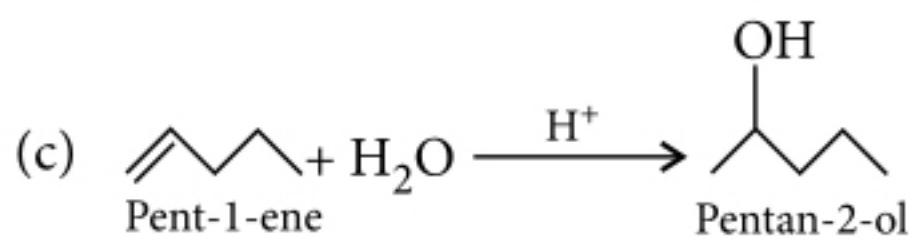
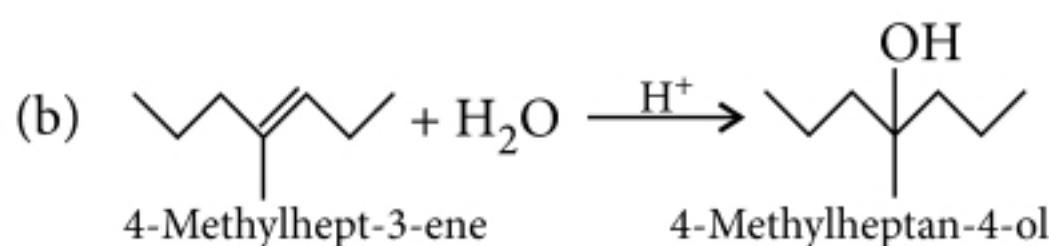
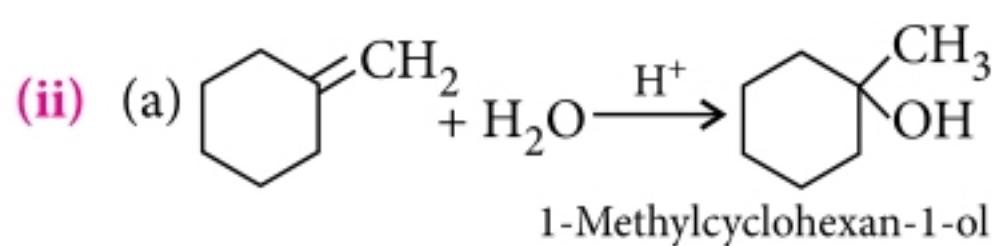
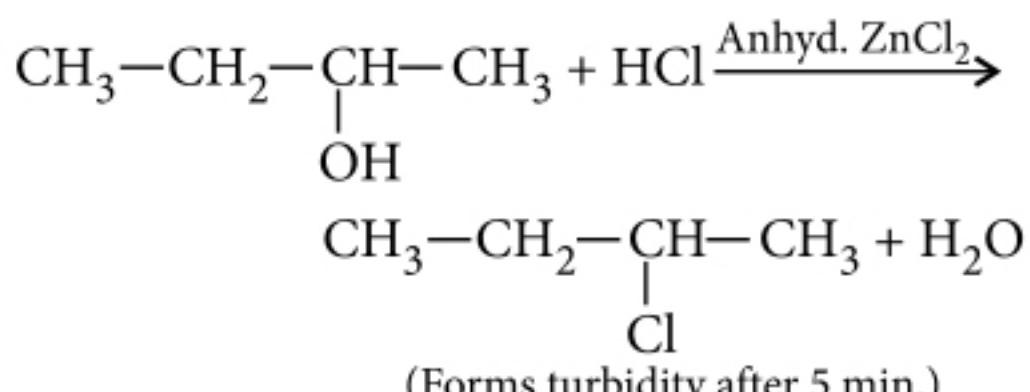
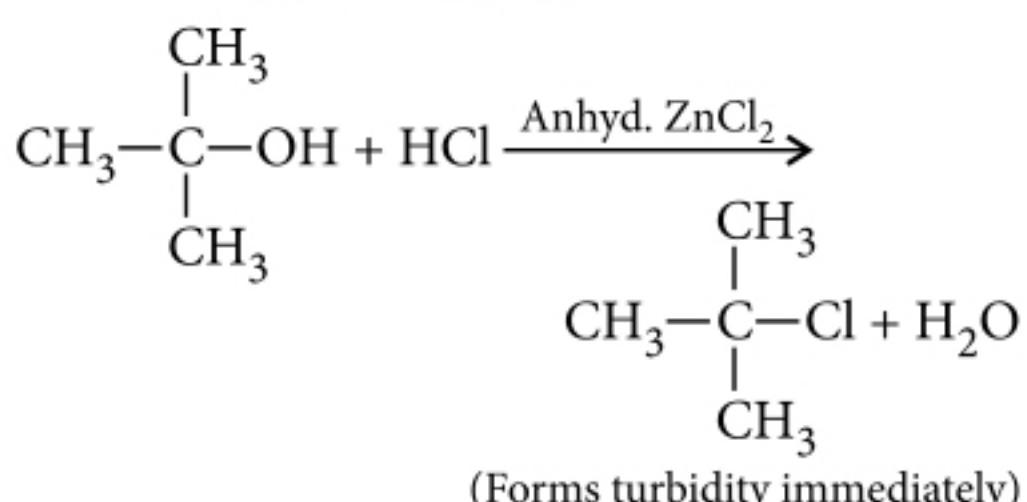
(iii) It is prepared in the laboratory by treating ethanol or acetone with iodine in presence of 5% NaOH.

(iv) Savlon is used as an antiseptic. It kills bacteria, fungi, insect larvae and worms much more effectively than iodoform. It also does not smell at all.

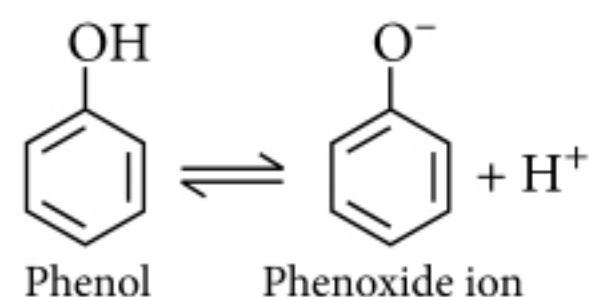
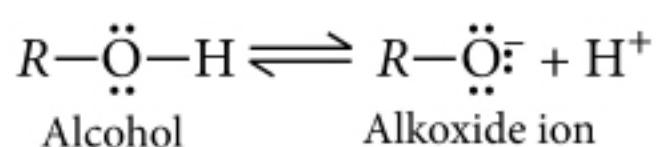
- 24. (i)** (a) Phenol gives violet coloured complex with neutral FeCl_3 solution while benzyl alcohol does not.



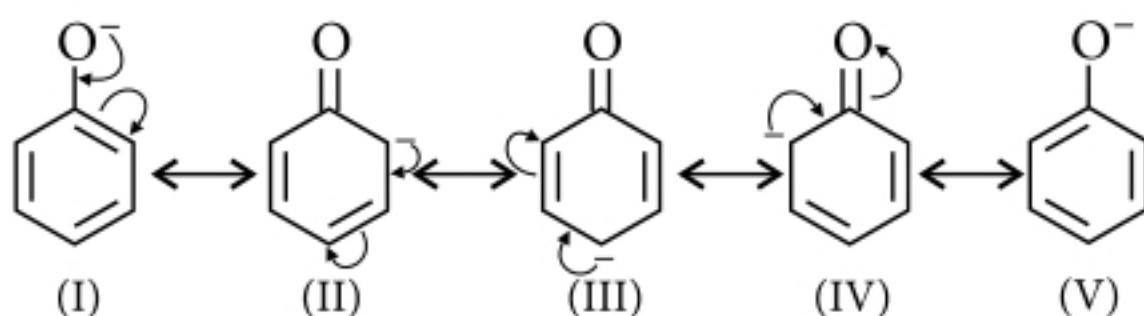
- (b) 2-Methylpropan-2-ol (tertiary alcohol) will give turbidity immediately when treated with Lucas' reagent (conc. HCl and anhyd. $ZnCl_2$) while butan-2-ol (secondary alcohol) will give turbidity after 5 minutes.



(i) (a) Phenols are more acidic than alcohols. It can be explained on the basis that alcohol on losing H^+ ions forms alkoxide ion and phenol forms phenoxide ion.



The greater acidity of phenol is due to the stability of the phenoxide ion which is resonance stabilized as shown below:

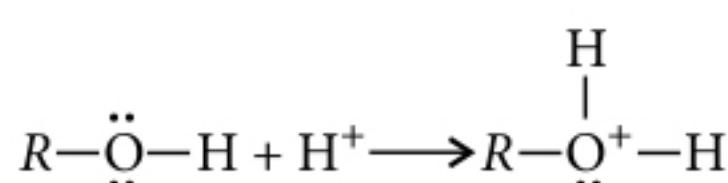


- (b) The boiling points of ethers are much lower than those of alcohols of comparable molar masses because unlike alcohols they cannot form intermolecular hydrogen bonds.

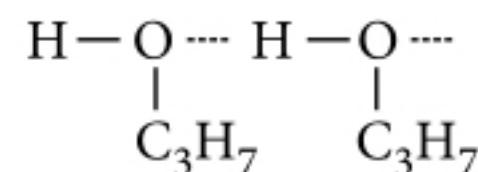
(iii) (a) In substituted phenols, the presence

- (ii) (a) In substituted phenols, the presence of electron releasing group decreases the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para*-positions. It is due to the increased negative charge in phenoxide ion. Thus *m*-aminophenol is stronger acid than *o*-aminophenol.

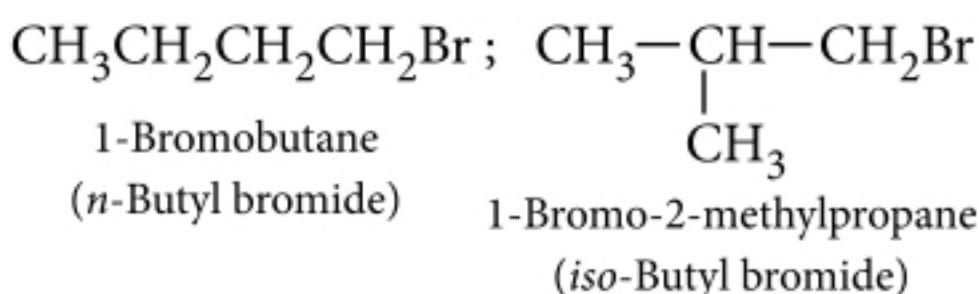
- (b) Alcohols act as weak base because of the presence of lone pairs of electrons on oxygen atom. H^+ ions from an acid adds on to oxygen of $\text{O} - \text{H}$ bond forming an oxonium ion.



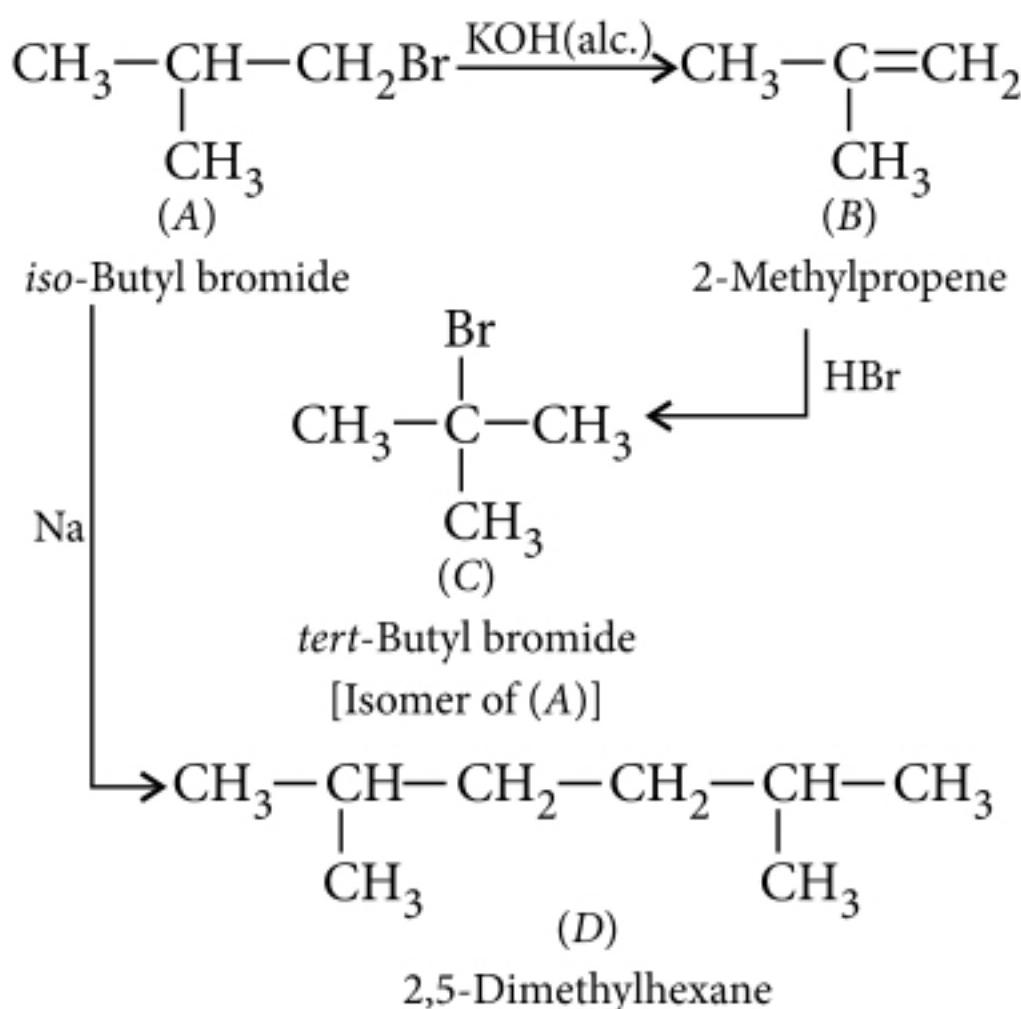
- (c) The molecules of butane are held together by weak van der Waals forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonding.



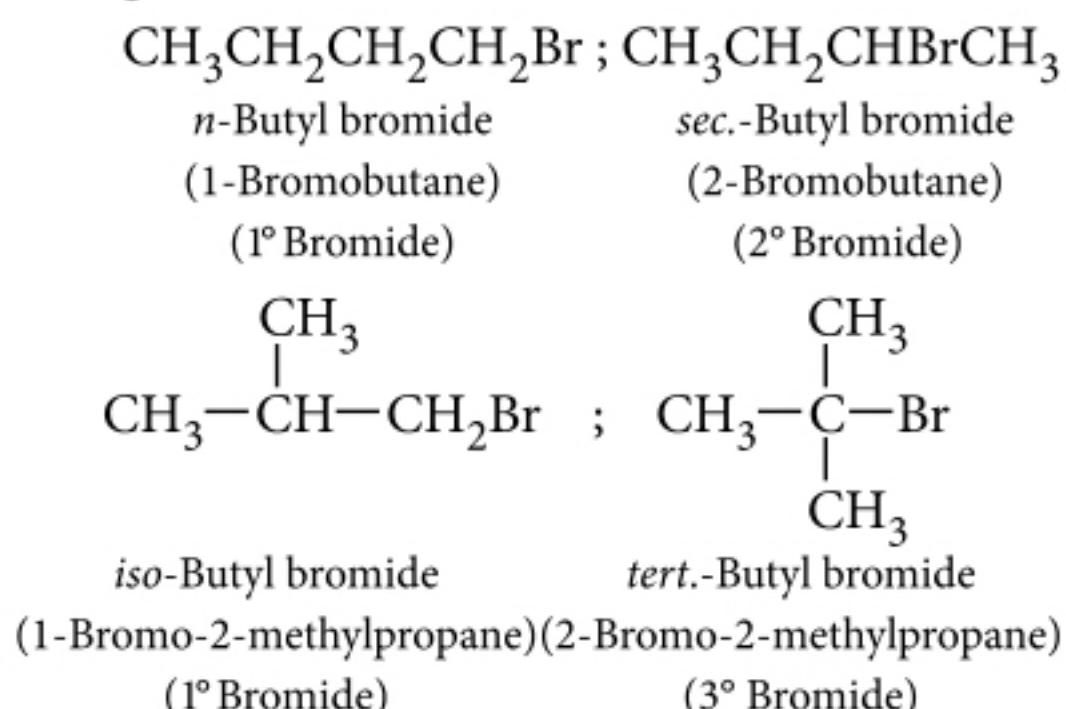
- 25. (i)** There can be only two primary alkyl bromides with molecular formula, C_4H_9Br . These are



(A) must be *iso*-butyl bromide as, when treated with sodium it gave a compound different than that produced by *n*-butyl bromide which reacts with sodium to give *n*-octane.



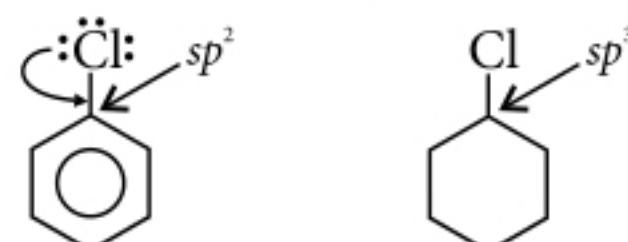
(ii) The isomers of the compound having molecular formula $\text{C}_4\text{H}_9\text{Br}$ along with their common and IUPAC names are given below:



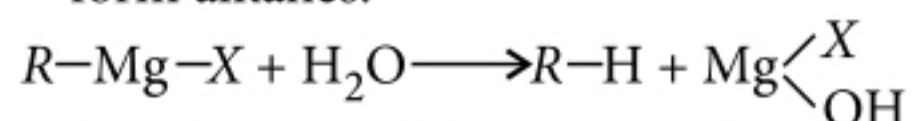
OR

(i) (a) There are two reasons : (i) In case of chlorobenzene, carbon to which chlorine is attached is sp^2 hybridised and is more electronegative than the corresponding carbon in cyclohexyl chloride which is sp^3 hybridised. So

the net dipole moment is lower in chlorobenzene. (ii) In chlorobenzene C — Cl bond has some double bond character so its bond length is smaller. Hence dipole moment is smaller than cyclohexyl chloride which has a longer C — Cl single bond.

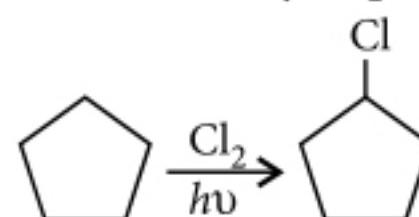


- (b) Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H — bond among water molecules is much higher than energy released by water halide interaction.
- (c) Grignard reagents react with water to form alkanes.

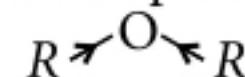


So, they must be prepared under anhydrous conditions.

(ii) Molecular formula C_5H_{10} indicates that it can be either an alkene or a cycloalkane. Since it does not react with chlorine in dark so it cannot be an alkene. It gives only a single monochloro derivative, which shows that all the hydrogen atoms are identical. It is a cycloalkane, i.e., cyclopentane.

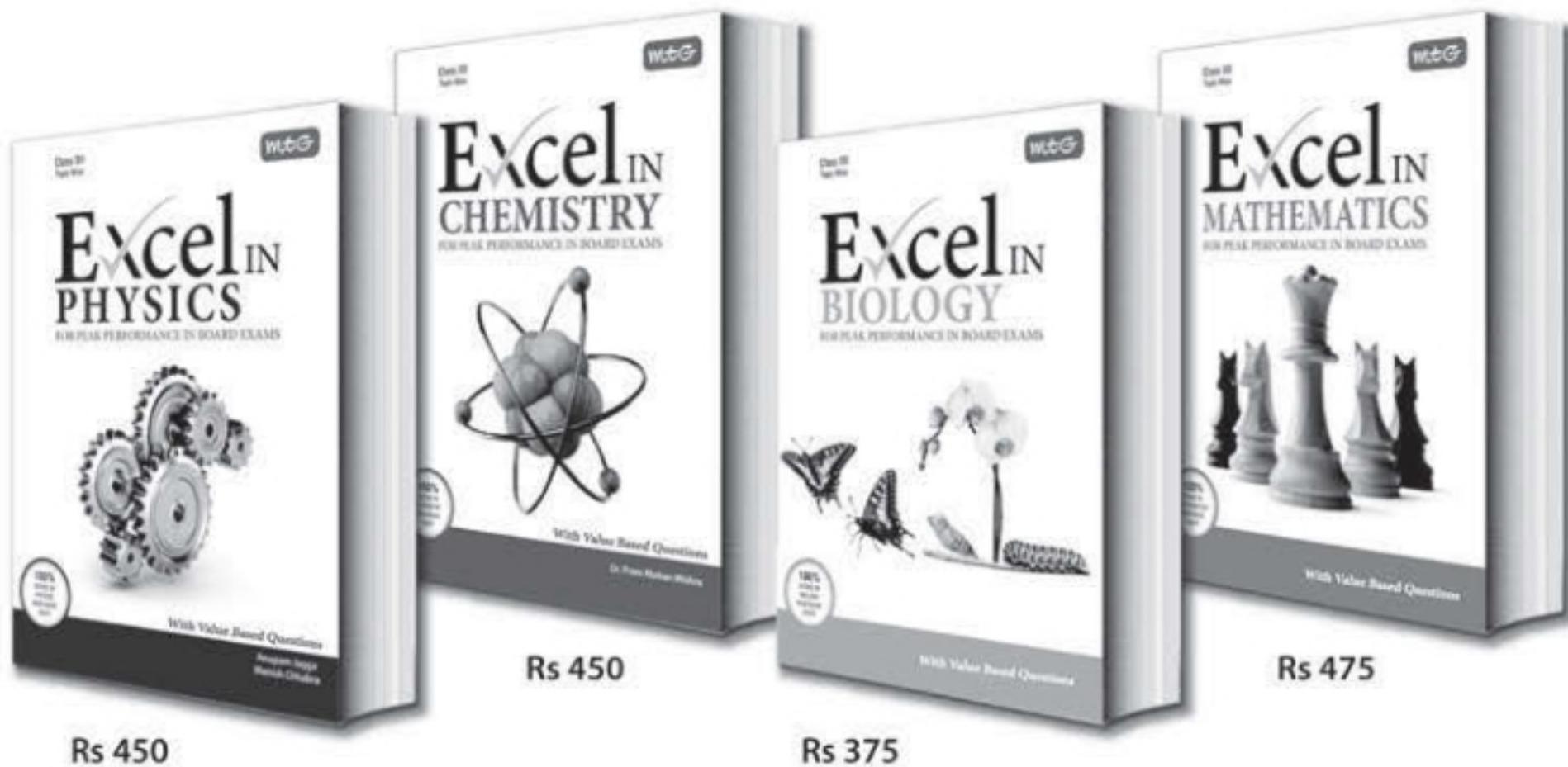


26. (i) (a) Due to the bent structure of ethers and polarity of C — O bond, all ethers have a net dipole moment.



- (b) As we know that the electron withdrawing groups enhance the acidic character of phenols because they help in the stabilisation of phenoxide ion. Nitro group is an electron withdrawing group whereas methoxy group is an electron releasing group, so *o*-nitrophenol is more acidic than *o*-methoxyphenol.

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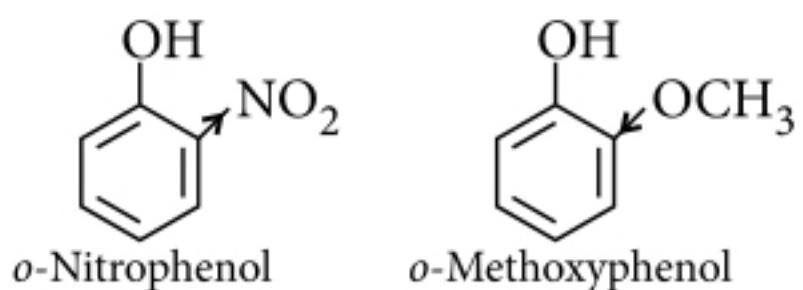


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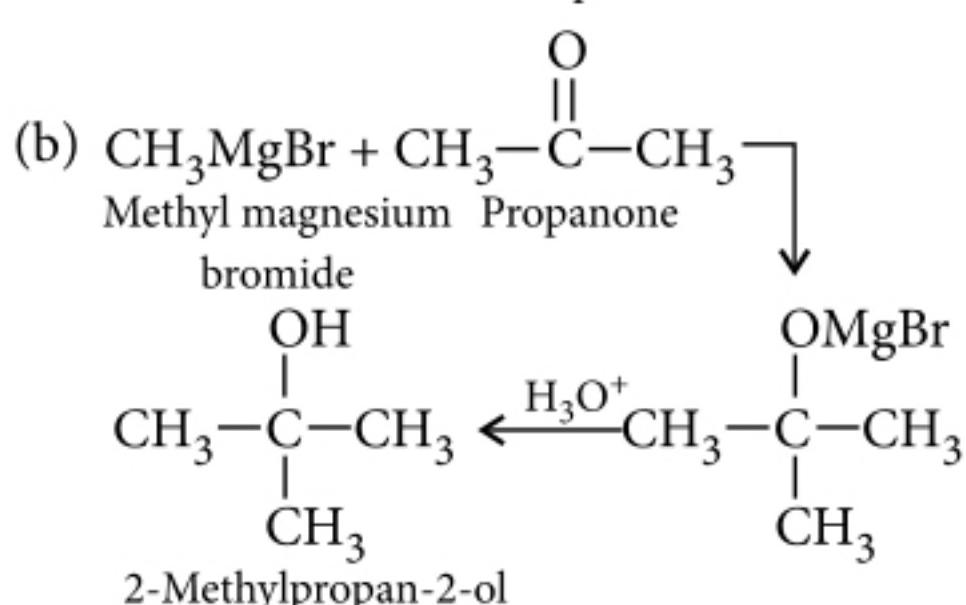
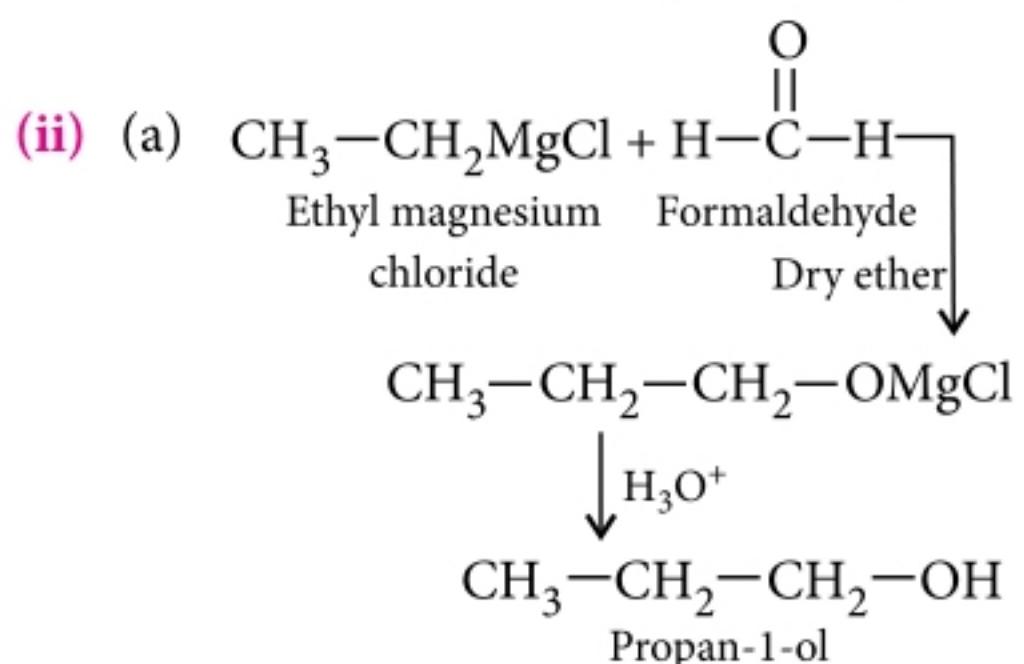
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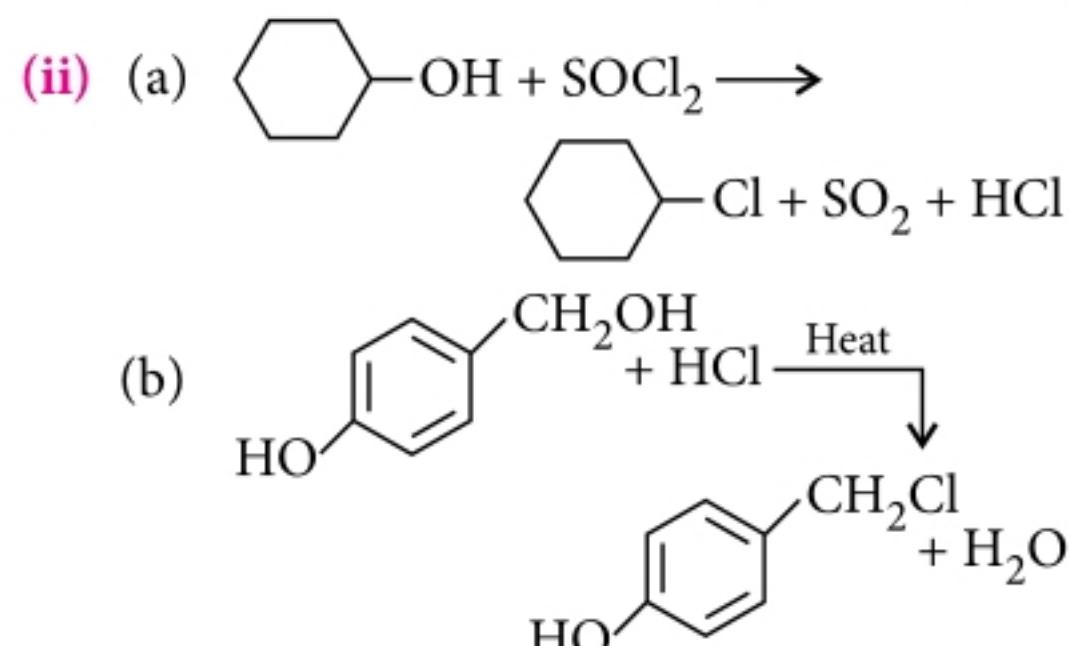
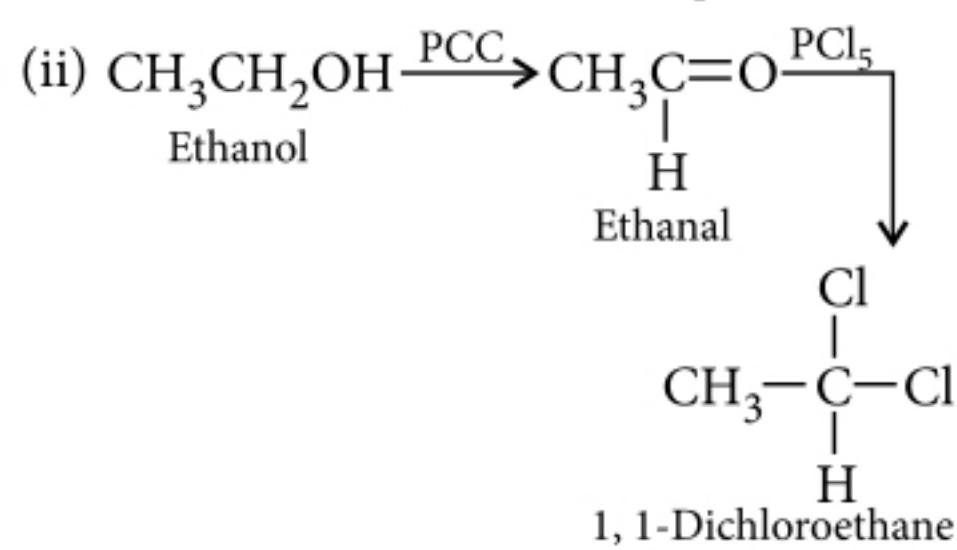
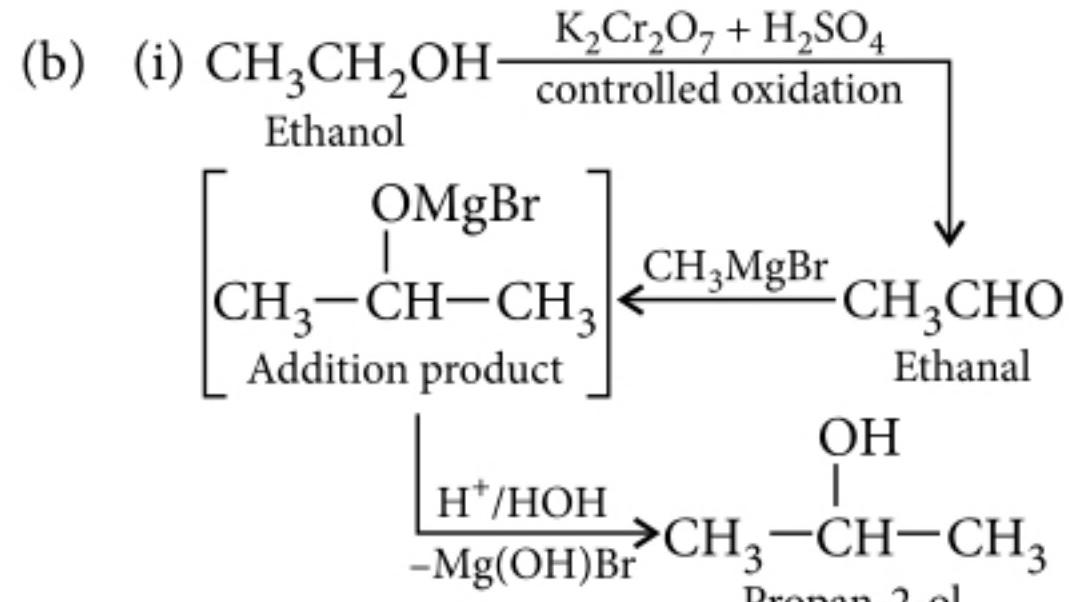
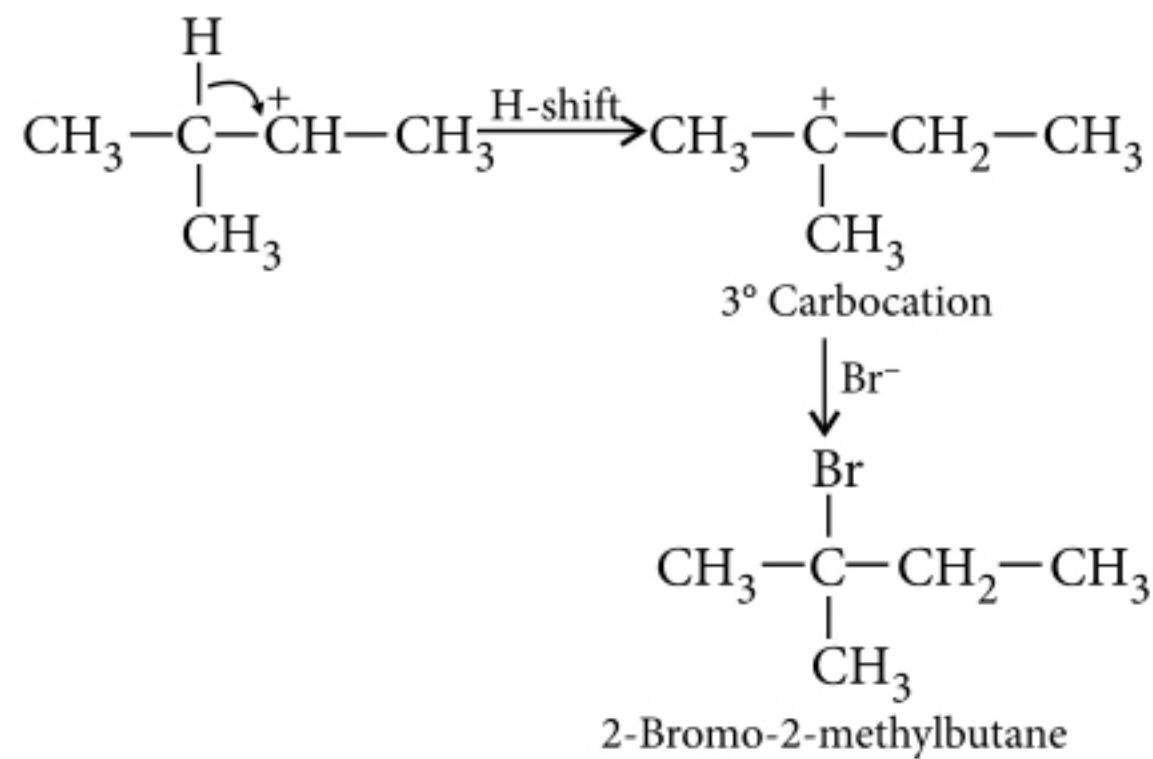
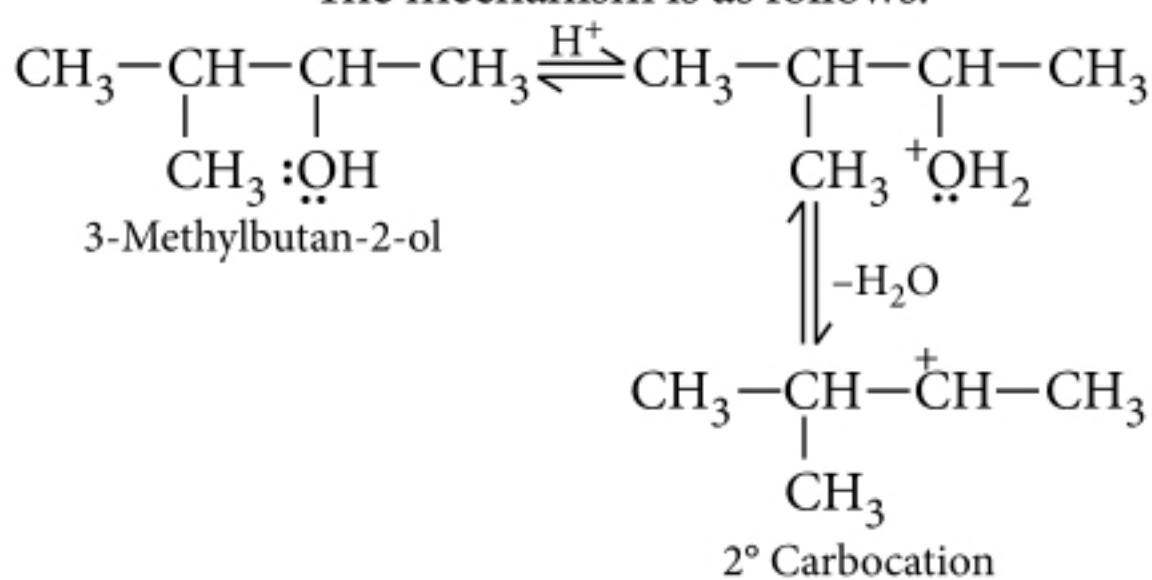


- (c) Alkyl groups have $+I$ effect. As the number of alkyl groups increases from primary to tertiary, electron density in the O—H bond is maximum in case of tertiary alcohol and minimum in case of primary alcohol. Thus, the O—H bond in tertiary alcohol is the strongest and in primary alcohol it is weakest. Thus, the acidity of alcohols follows the order primary > secondary > tertiary.



OR

- (i) (a) This reaction proceeds through the rearrangement of the 2° carbocation formed into a more stable 3° carbocation. The mechanism is as follows:



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EXAMINER'S MIND NCERT CLASS XII

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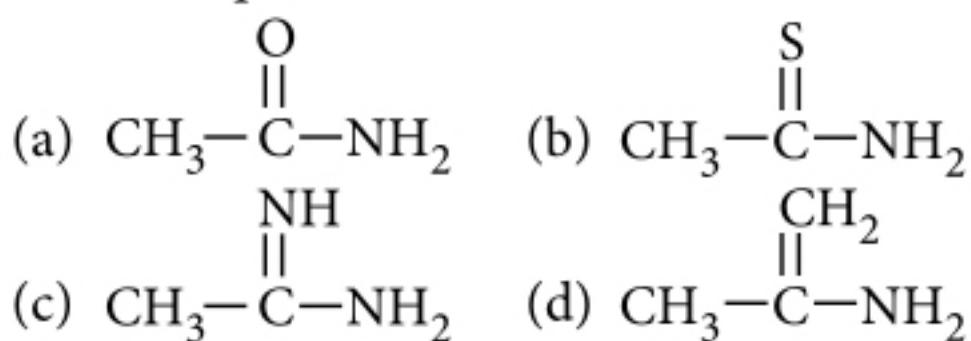
AMINES | BIOMOLECULES

SECTION - I

Only One Option Correct Type

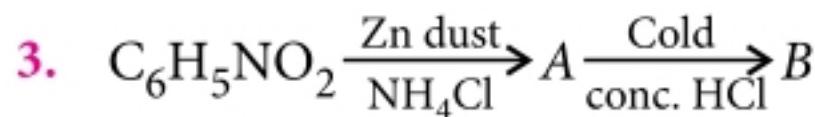
This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- 1.** Which of the following compounds is the most basic in aqueous medium?



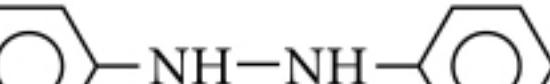
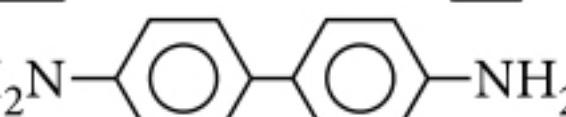
- 2.** Mixture of 1° , 2° and 3° amines can be separated by

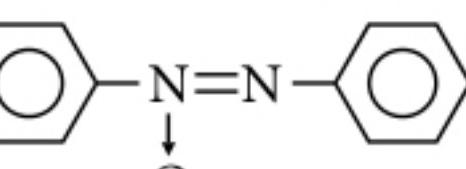
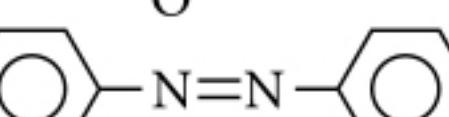
- (a) Hinsberg's method
 - (b) Hofmann's method
 - (c) distillation
 - (d) all of the above.



A and *B* respectively are

- (a)  NHOH, 

(b) 


(c) 


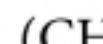
(d) None is correct.

4. Maximum pK_b value is of

- (a) 

(b) $(\text{CH}_3\text{CH}_2)_2\text{NH}$

(c) $(\text{CH}_3)_2\text{NH}$

(d) 

- 5. Which is the best leaving group?**

6. Which one of the following sets of monosaccharides forms sucrose?

- (a) α -D-galactopyranose and α -D-glucopyranose
 - (b) α -D-glucopyranose and β -D-fructofuranose
 - (c) β -D-glucopyranose and α -D-fructofuranose
 - (d) α -D-glucopyranose and β -D-fructopyranose.

7. The shape of $(CH_3)_3N$ is pyramidal because

- (a) nitrogen forms three sp^3 hybridised sigma bonds with carbon atoms of methyl groups

- (b) nitrogen forms three sp^2 hybridised sigma bonds with carbon atoms of methyl groups and fourth orbital forms pi bond

- (c) nitrogen has five valencies which are arranged in pyramidal shape.
 - (d) the unpaired electron present on nitrogen is delocalised.

8. A dextrorotatory sugar present in fruits is
(a) glucose (b) fructose
(c) cellulose (d) starch

9. For the nitration of aniline, which of the following steps is followed?

- (a) Direct nitration using nitrating mixture (conc. HNO_3 + conc. H_2SO_4) followed by oxidation.

(b) Using fuming HNO_3 at 273 K followed by hydrolysis.

(c) Using NaNO_2 and HCl followed by reaction with conc. HNO_3 followed by hydrolysis.

(d) Acetylation followed by nitration and hydrolysis.

10. Which of the following statements about RNA is not correct?

(a) It has a single strand.

(b) It does not undergo replication.

(c) It does not contain any pyrimidine base.

(d) It controls the synthesis of proteins.

11. The reaction of benzenesulphonyl chloride with ethylamine yields

(a) N -ethylbenzenesulphonamide, insoluble in alkali

(b) N,N -diethylbenzenesulphonamide, soluble in alkali

(c) N,N -diethylbenzenesulphonamide, insoluble in alkali

(d) N -ethylbenzenesulphonamide, soluble in alkali.

12. Five-membered ring structures of fructose are given below. Mark the incorrect statement.

(a) The five-membered ring structures are named as furanose structures.

(b) The cyclic structures represent two anomers of fructose.

(c) Five-membered ring structures are named as pyranose structures.

(d) These are also called Haworth structures.

13. Which of the following is not a property of diazonium salts?

(a) Diazonium salts are colourless, crystalline solids.

(b) Being ionic in nature they are soluble in water.

(c) Most of these salts explode when dried.

(d) The aqueous solutions of these salts are poor conductors of electricity.

14. A tripeptide is composed equally of *L*-valine, *L*-tyrosine and *L*-alanine (one molecule of each). How many isomeric tripeptides of this kind may exist?

(a) 3 (b) 4

(c) 6 (d) 8

15. Which of the following compounds cannot be identified by carbylamine test?

(a) $\text{CH}_3\text{CH}_2\text{NH}_2$ (b) $(\text{CH}_3)_2\text{CHNH}_2$

(c) $\text{C}_6\text{H}_5\text{NH}_2$ (d) $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_5$

16. Which of the following acids is a vitamin?

(a) Aspartic acid (b) Adipic acid

(c) Ascorbic acid (d) Saccharic acid

17. Which of the following is amphoteric in nature?

(a) CH_3NH_2 (b) CH_3NHCH_3

(c) CH_3CONH_2 (d) $\text{CH}_3-\underset{\text{CH}_3}{\text{N}}-\text{CH}_3$

18. Milk changes after digestion into

(a) glucose (b) lactose

(c) fructose (d) glycogen.

19. Which of the following is correct method to convert *p*-toluidine to *p*-toluic acid?

(a) Diazotisation, CuCN , H_2/Pd

(b) $\text{CHCl}_3/\text{NaOH}$, KCN , Sn/HCl

(c) Diazotisation, CuCN/KCN , $\text{H}_2\text{O}/\text{H}^+$

(d) Diazotisation, NaCN , NaOH

20. Keratin, a structural protein is present in

(a) hair (b) wool

(c) silk (d) all of these.

SECTION - II

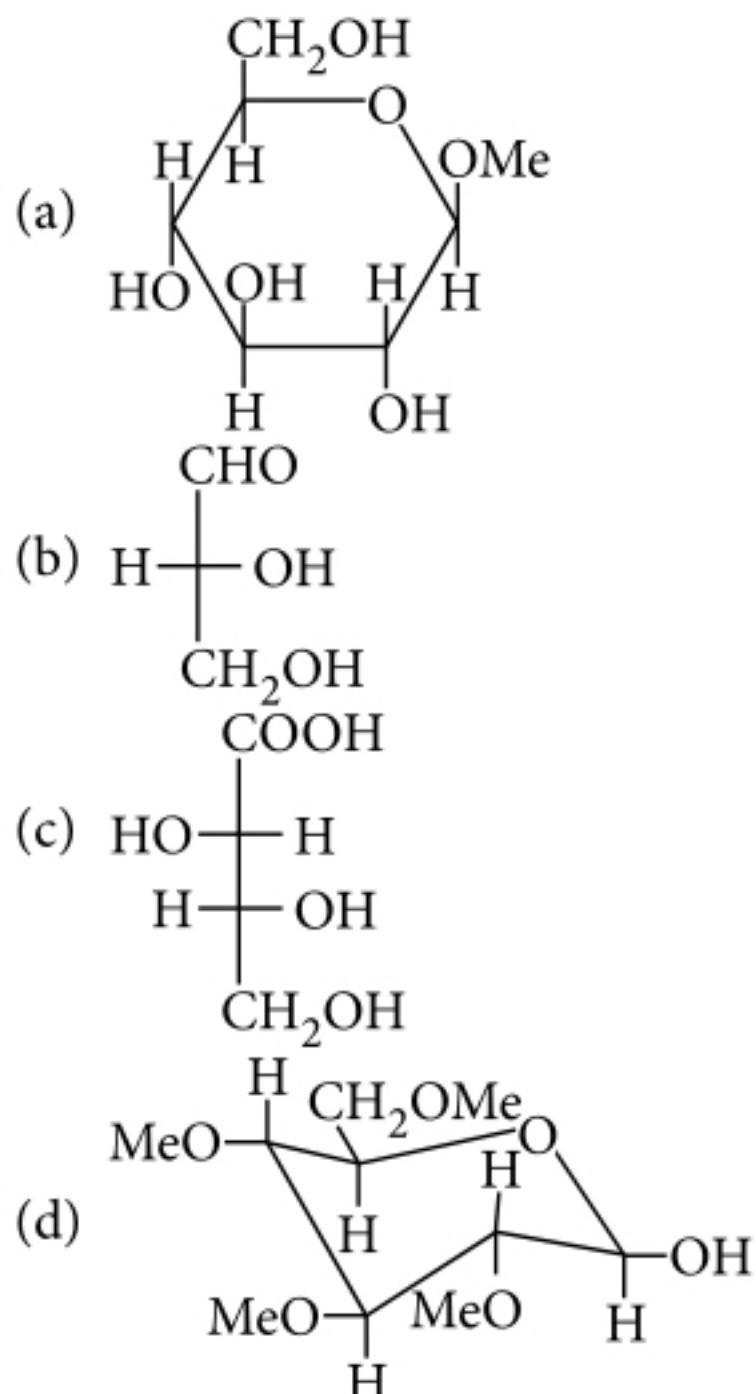
One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

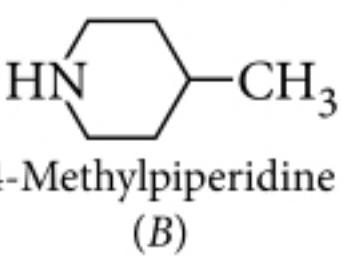
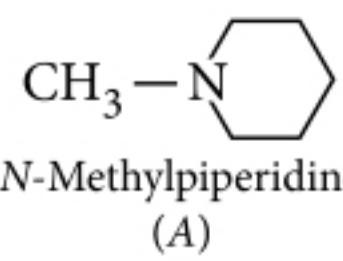
- 21.** Select the correct statement(s).

 - (a) Most alkylamines are more basic than ammonia in aqueous solution.
 - (b) pK_a of $\text{Me}_3\overset{+}{\text{NH}}$ is higher than that of $\overset{+}{\text{NH}}_4$.
 - (c) Aniline is more stable than anilinium ion.
 - (d) pK_b of CH_3NH_2 is higher than that of NH_3 .

22. Which of the following carbohydrates are D-isomers?

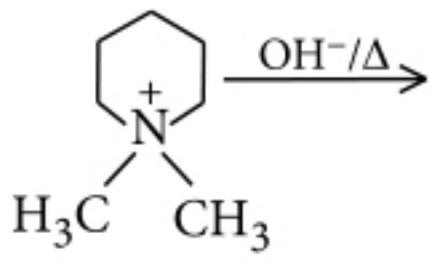


23. Which of the following statement(s) is/are correct.



- (a) A has higher boiling point than B.
- (b) B has higher boiling point than A.
- (c) A and B have same boiling point being isomeric amines.
- (d) B reacts with benzenesulphonyl chloride while A does not.

24. In the following reaction,



the product(s) is/are

- (a)
- (b)
- (c)
- (d)

25. $D-(+)-\text{Glucose} \xrightarrow{5(\text{CH}_3\text{CO})_2\text{O}} D-(+)-\text{Glucose}$
pentaacetate

Which statement(s) is/are true about glucose pentaacetate?

- (a) It will react with phenylhydrazine but not with Tollens' reagent.
- (b) It will react with Tollens' reagent but not with phenylhydrazine.
- (c) It will react with both of the above mentioned reagents.
- (d) It will react neither with phenylhydrazine nor with Tollens' reagent.

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

Proteins are the polymers of about twenty different α -amino acids which are linked by peptide bonds. Ten amino acids are called essential amino acids because they cannot be synthesised by our body, hence must be provided through diet. Proteins perform various structural and dynamic functions in the organisms. Proteins which contain only α -amino acids are called simple proteins. The secondary or tertiary structure of proteins get disturbed on change of pH or temperature and they are not able to perform their functions. This is called denaturation of proteins.

26. Which of the following α -amino acids does not form optical isomers?

- (a) $\overset{+}{\text{NH}_3}\text{CH}(\text{CH}_3)\text{COO}^-$
- (b) $\overset{+}{\text{NH}_3}\text{CH}_2\text{COO}^-$
- (c) $\overset{+}{\text{NH}_3}\text{CH}(\text{CH}_2\text{Ph})\text{COO}^-$
- (d) $\overset{+}{\text{NH}_3}\text{CH}(\text{CH}(\text{CH}_3)_2)\text{COO}^-$

27. Which of the following amino acids contain sulphur and is an essential amino acid?

- (a) Isoleucine
- (b) Methionine
- (c) Proline
- (d) Glutamine

28. Which of the following statements is incorrect regarding digestion of proteins?

- (a) Proteins are hydrolysed to peptones in mouth by amylase.
- (b) Proteins are hydrolysed to peptones in stomach by pepsin.

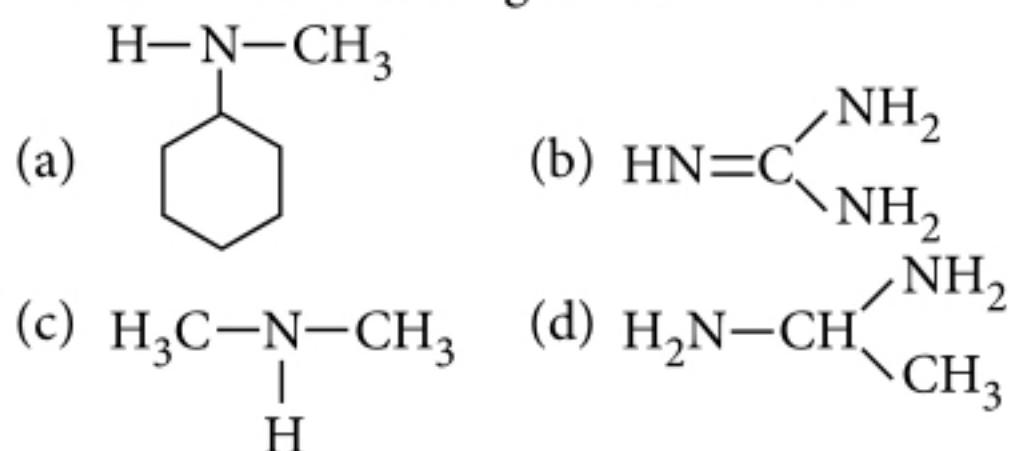
- (c) The peptones are broken to peptides in the intestine by trypsin.
 (d) The peptides are further broken to amino acids in the intestine by peptidase.

Paragraph for Questions 29 to 31

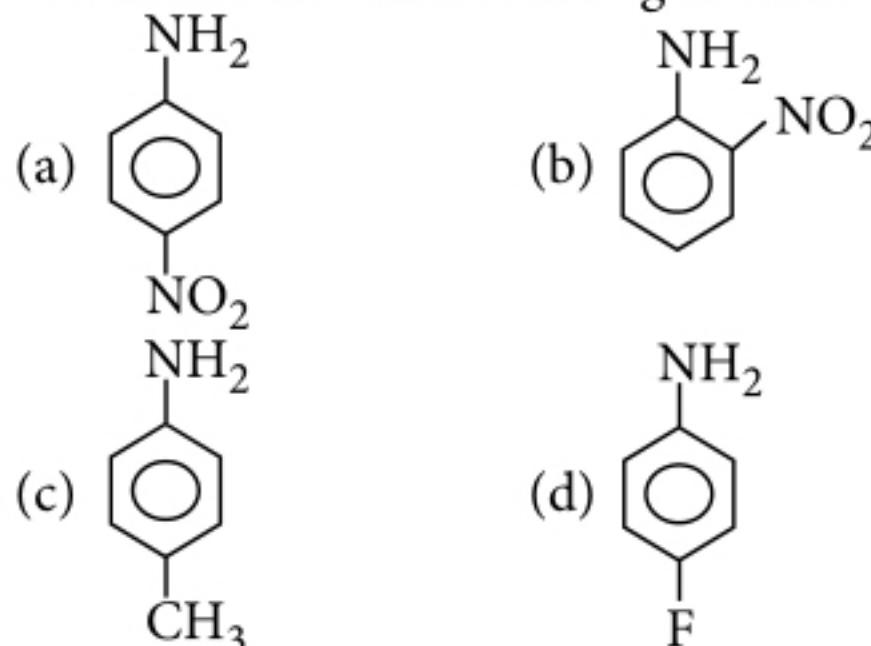
All amines are basic in nature due to the presence of lone pair on nitrogen atom. Aliphatic amines are more basic than ammonia and aromatic amines but aromatic amines are less basic than ammonia. This is due to (+I) effect of alkyl group and resonance effect of benzene ring. In aromatic amines, presence of electron withdrawing group decreases basic character and electron donating group increases basic character.

- 29.** Which of the following is least basic?
 (a) *o*-Toluidine (b) *N*-Methylaniline
 (c) *m*-Toluidine (d) *p*-Toluidine

- 30.** Which of the following is most acidic?



- 31.** The most basic amine among the following is



SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- 32.** Match the List I with List II and select the correct answer using the code given below the lists :

	List I		List II
P.	Benzenesulphonyl chloride	1.	Zwitter ion
Q.	Sulphanilic acid	2.	Hinsberg's reagent
R.	Alkyldiazonium salts	3.	Dyes
S.	Aryldiazonium salts	4.	Conversion to alcohols

P	Q	R	S
(a) 4	1	2	3
(b) 3	2	4	1
(c) 2	1	4	3
(d) 4	2	3	1

- 33.** Match the List I with List II and select the correct answer using the code given below the lists :

	List I		List II
P.	Peptide linkage	1.	Inversion
Q.	Nucleic acid	2.	Polysaccharide
R.	Hydrolysis of cane sugar	3.	Proteins
S.	Starch	4.	Nucleotides

P	Q	R	S
(a) 2	1	3	4
(b) 4	1	2	3
(c) 3	4	1	2
(d) 1	3	4	2

- 34.** Match the List I with List II and select the correct answer using the code given below the lists :

	List I		List II
P.	Reaction of benzene-diazonium chloride with cuprous salts dissolved in the halogen acid.	1.	Gattermann reaction
Q.	Reaction of benzenediazonium chloride with halogen acid in the presence of copper powder.	2.	Sandmeyer reaction
R.	Reaction of amines with chloroform.	3.	Hinsberg's reaction
S.	Reaction of amines with benzenesulphonyl chloride.	4.	Carbylamine reaction

P	Q	R	S
(a) 1	2	3	4
(b) 4	3	2	1
(c) 3	4	1	2
(d) 2	1	4	3

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.

35. Assertion : Proteins are made up of α -amino acids.

Reason : During denaturation, secondary and tertiary structures of proteins are destroyed.

36. Assertion : Gabriel phthalimide synthesis can be used to convert alkyl chlorides into primary amines.

Reason : With proper choice of reagent Gabriel synthesis can be used to prepare primary, secondary and tertiary amines.

37. Assertion : All enzymes are proteins but all proteins are not enzymes.

Reason : Enzymes defend the body against the invasion of foreign organisms.

38. Assertion : The amino group of aniline being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

Reason : In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

39. Assertion : All enzymes found in cells are invariably proteins which catalyse biological reactions.

Reason : Enzymes act efficiently at a moderate temperature and pH.

40. Assertion : *p*-Methoxyaniline (*p*-anisidine) is a stronger base than *m*-Methoxyaniline (*m*-anisidine).

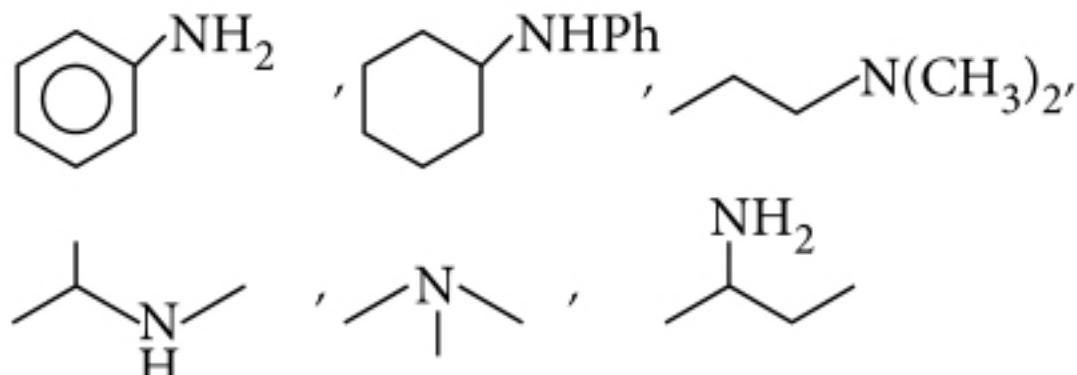
Reason : At *m*-position, methoxy group can exert only $-I$ effect but not $+R$ effect.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. Number of amines out of the following which will react with CS_2 is

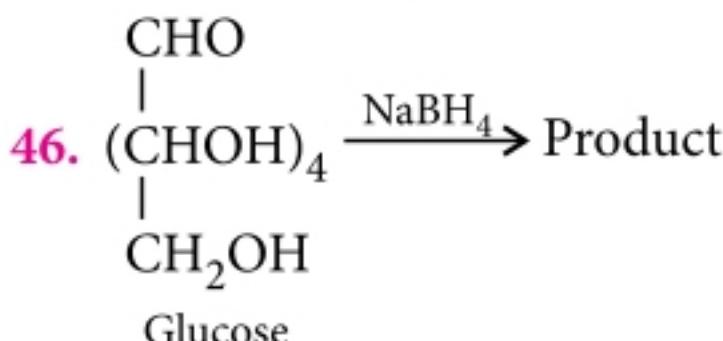


42. Glucose reacts with x moles of phenylhydrazine to yield osazone. The value of x is

43. $\text{C}_4\text{H}_{11}\text{N}$ on reaction with HNO_2 forms 3° alcohol. Thus, amine is x° . x is _____.

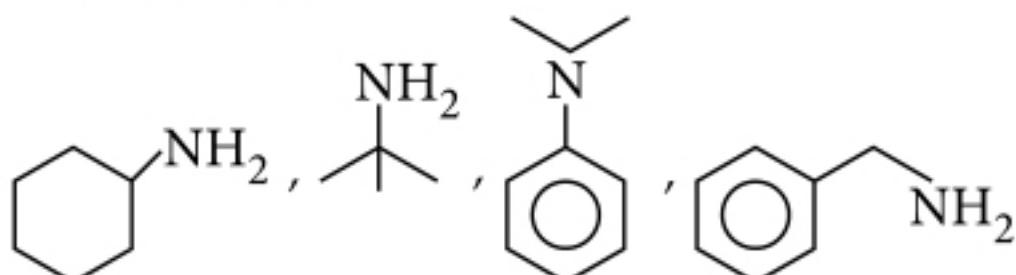
44. In sucrose, two monosaccharides are held together by a glycosidic linkage between C-1 of α -glucose and C_x of β -fructose. Here x is

45. Liebermann's nitroso reaction is given by x° amines only. The value of x is



Number of possible racemic forms of the product is

47. Number of compounds out of the following which will react with HNO_2 by formation of C—N bond is

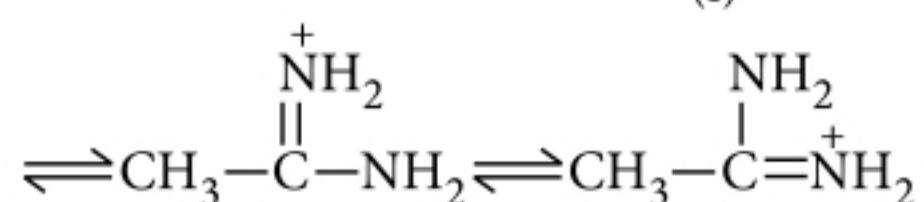
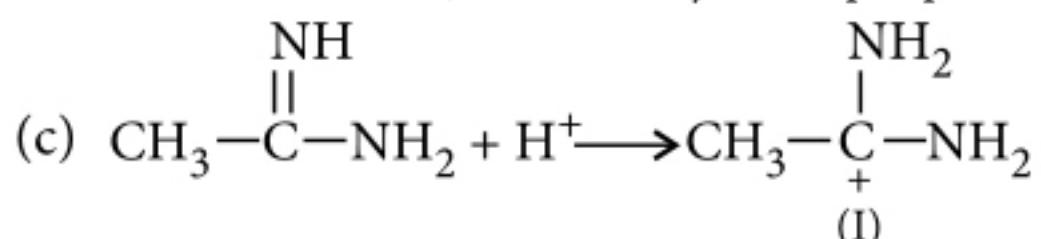
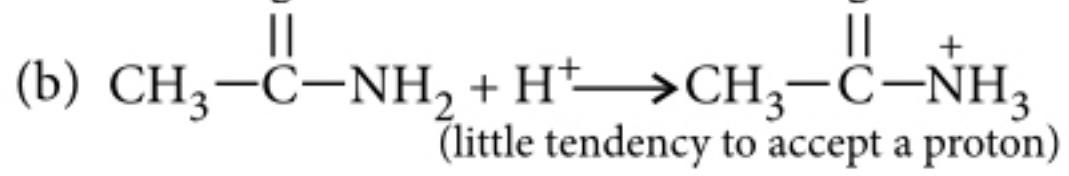
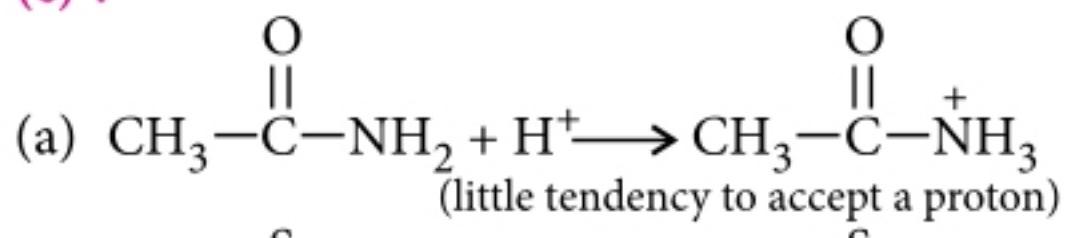


48. α - and β -D-glucose differ in configuration at anomeric carbon at carbon position number _____.

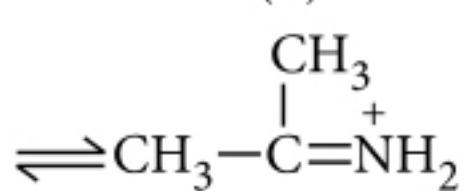
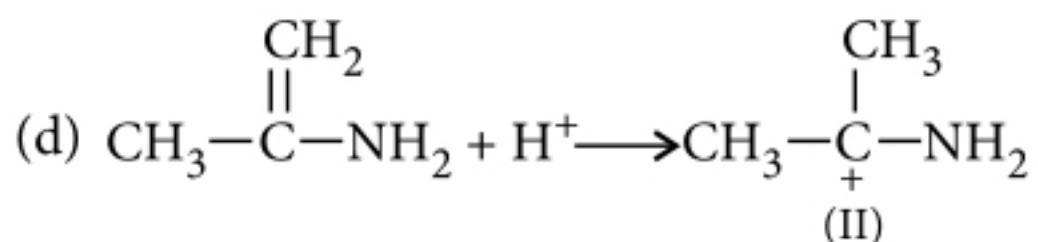
49. In carbylamine reaction, number of molecules of alcoholic KOH used is
50. Fructose is subjected to bond cleavages by HIO_4 . The number of HCHO unit(s) formed per unit of fructose is _____.

SOLUTIONS

1. (c) :



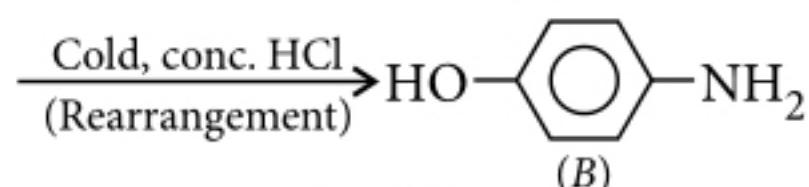
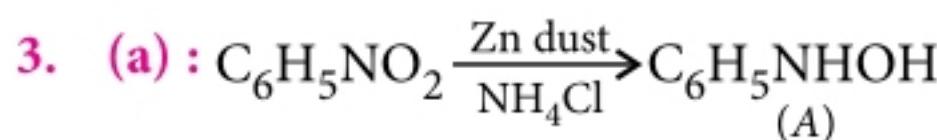
Carbocation (I) is more stable since it has two equivalent resonance structures.



Carbocation II is less stable than I since it has only one resonating structure.

Thus, compound (c) is most basic.

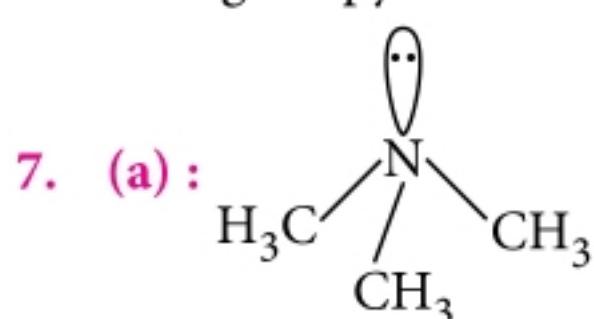
2. (d)



4. (d)

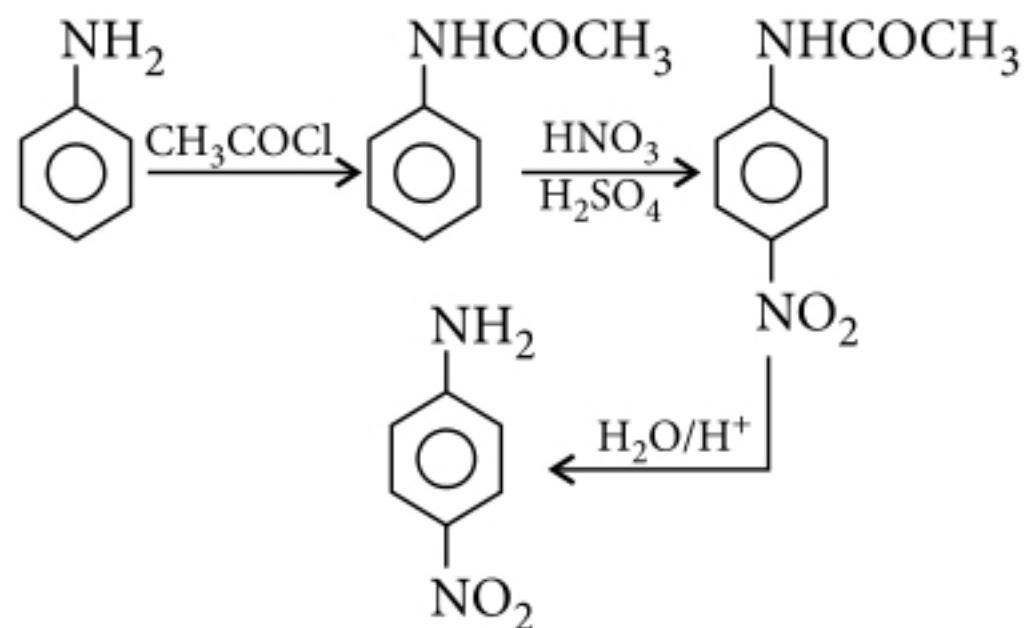
5. (a)

6. (b) : Sucrose is formed by the condensation of α -D-glucopyranose and β -D-fructofuranose.

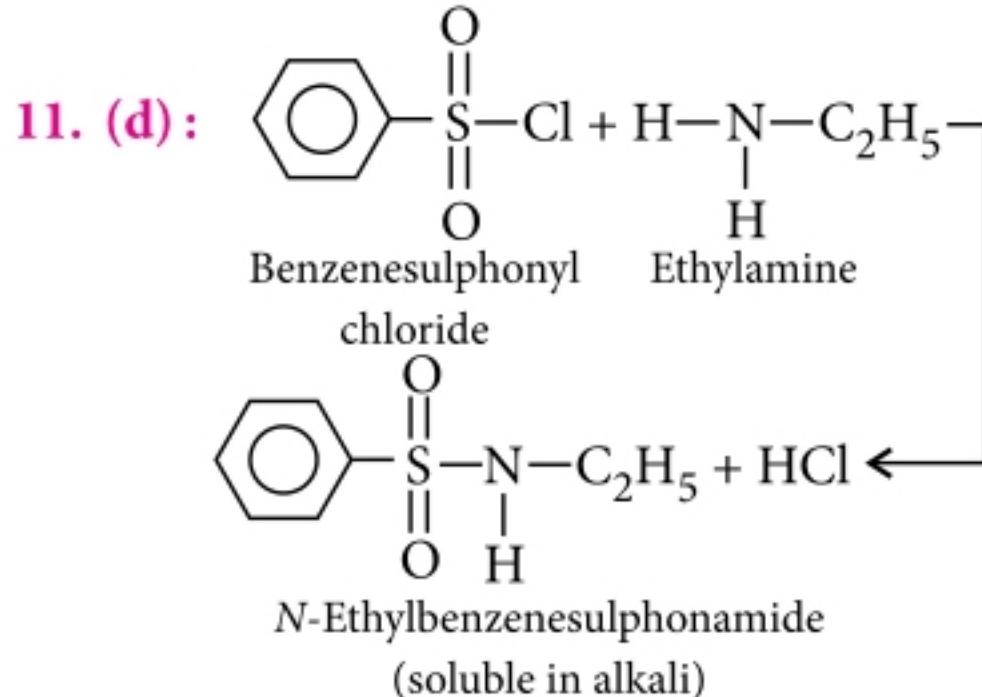


8. (a) : Glucose is dextrorotatory.

9. (d) : $-\text{NH}_2$ group is first oxidised on direct nitration hence $-\text{NH}_2$ group is first blocked by acetylation and then nitration is carried out.



10. (c) : It contains uracil and cytosine as pyrimidine bases. Therefore, statement (c) is wrong.



12. (c) : Five-membered rings are named as furanose while six-membered rings are named as pyranose rings.

13. (d) : The aqueous solutions of diazonium salts are good conductors of electricity.

14. (c) : Val. Tyr. Ala Tyr. Ala. Val
Val. Ala. Tyr Ala. Tyr. Val
Tyr. Val. Ala Ala. Val. Tyr

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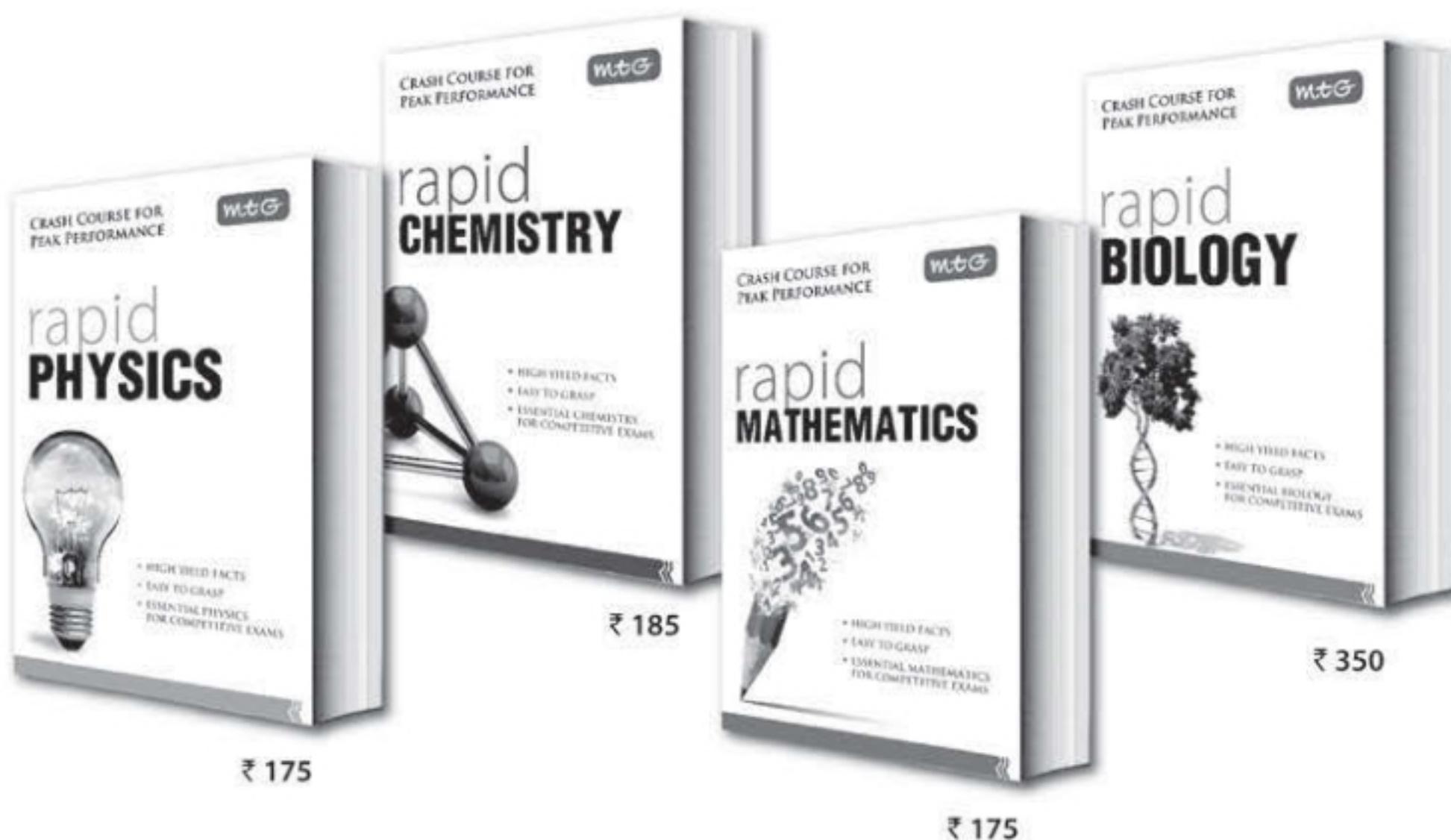
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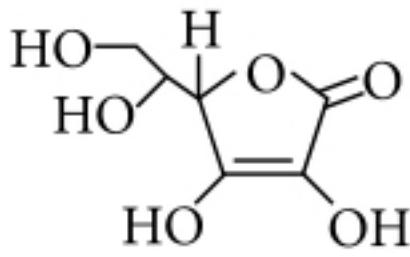


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15. (d) : Secondary amines do not give carbonylamine test.

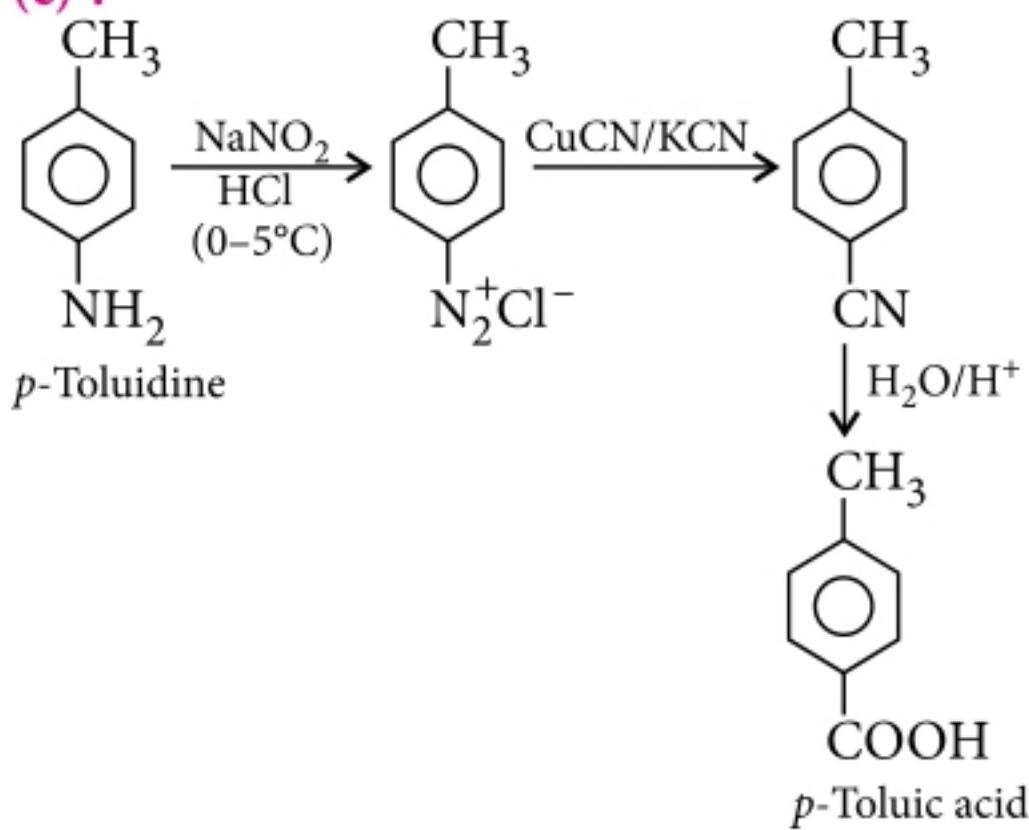
16. (c) : Ascorbic acid is vitamin C. Its structure is



17. (c) : Amines are basic in nature while amides are amphoteric in nature.

18. (a) : Milk contains lactose which on hydrolysis gives glucose and galactose.

19. (c) :

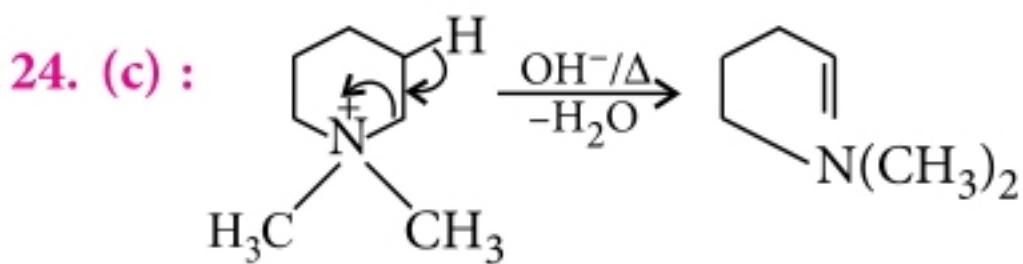


20. (d) : Keratin is a fibrous protein present in hair, wool, silk and muscles.

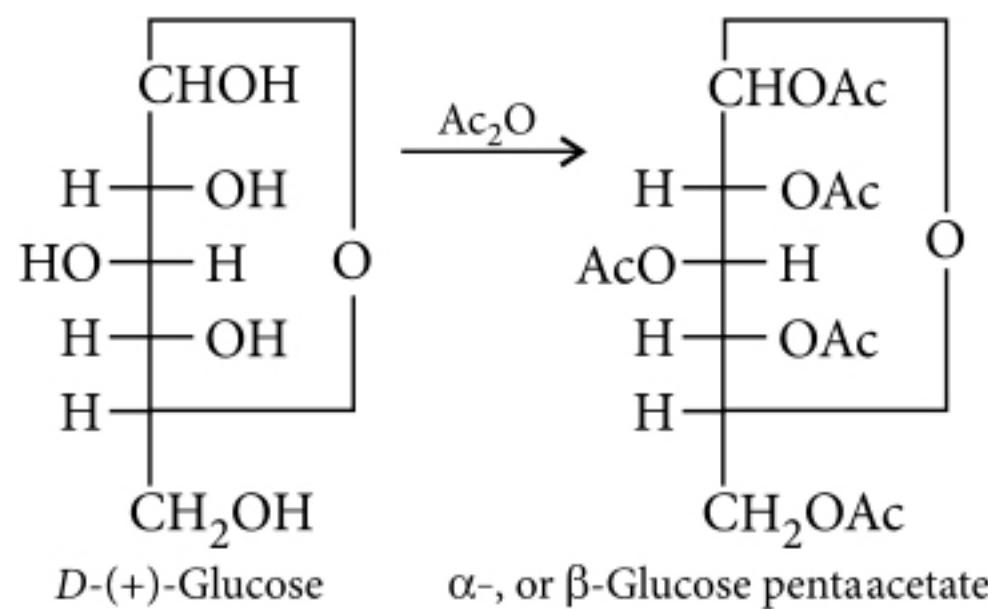
21. (a, b, c)

22. (a, b, c, d) : The compound whose numerically largest numbered (as per IUPAC convention) asymmetric carbon has configuration similar to *D*-glyceraldehyde has *D*-configuration.

23. (b, d)

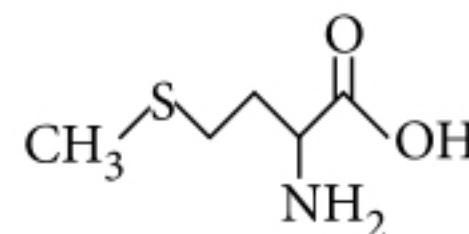


25. (d) : During acetylation of (+)-glucose, it is the C₁ — OH of the hemiacetal that is acetylated and not the C₅ — OH that forms the ring (cyclic structure). Since equilibrium with the open-chain aldehyde is prevented, the pentaacetate does not respond to the aldehydic reactions.



26. (b)

27. (b) : Methionine is an essential amino acid which contains sulphur.



28. (a) : Proteins $\xrightarrow[\text{(stomach)}]{\text{Pepsin + HCl}}$ Peptones

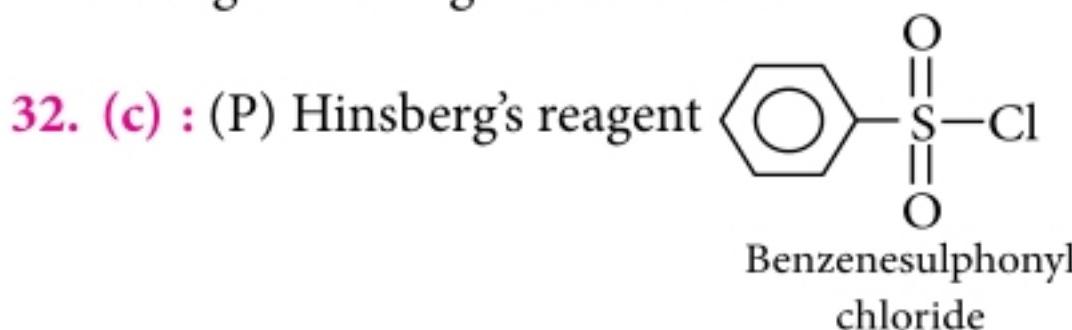
$\xrightarrow[\text{(intestine)}]{\text{Trypsin}}$ Peptides $\xrightarrow[\text{(intestine)}]{\text{Peptidase}}$ Amino acids

Hence choices (b), (c) and (d) are correct.
(a) is incorrect because in mouth by amylase only polysaccharides are hydrolysed to disaccharides.

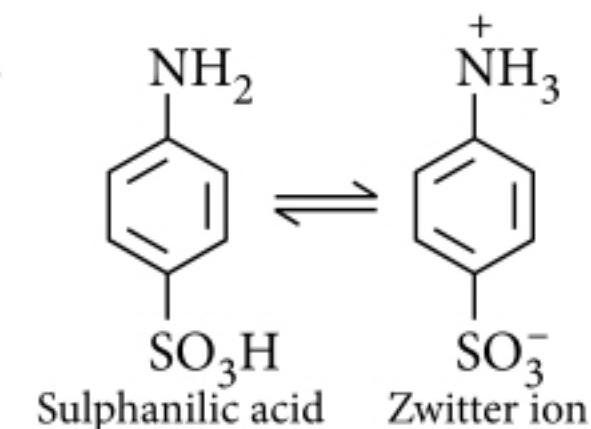
29. (a) : Due to *ortho*-effect, *o*-toluidine is the weakest base, even weaker than aniline.

30. (b)

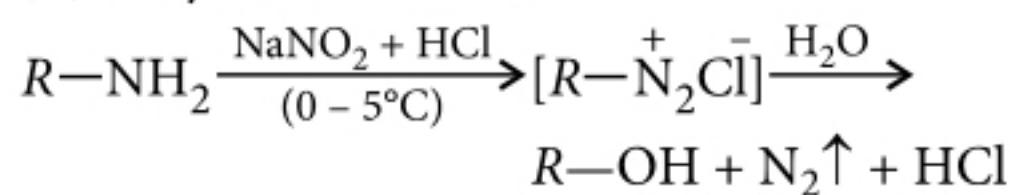
31. (c) : Only —CH₃ group is electron donating group hence it increases the electron density on nitrogen making it most basic.



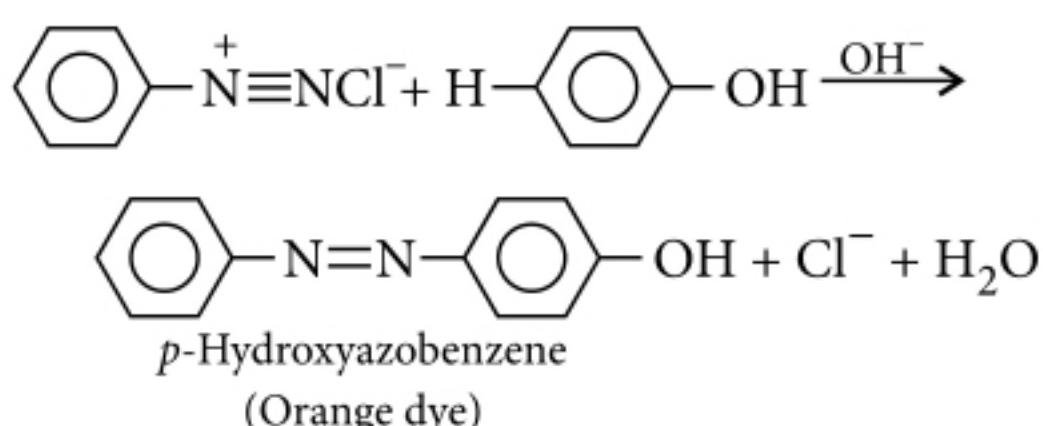
(Q) Sulphanilic acid



(R) Alkyldiazonium salts



(S) Aryldiazonium salts



33. (c) 34. (d)

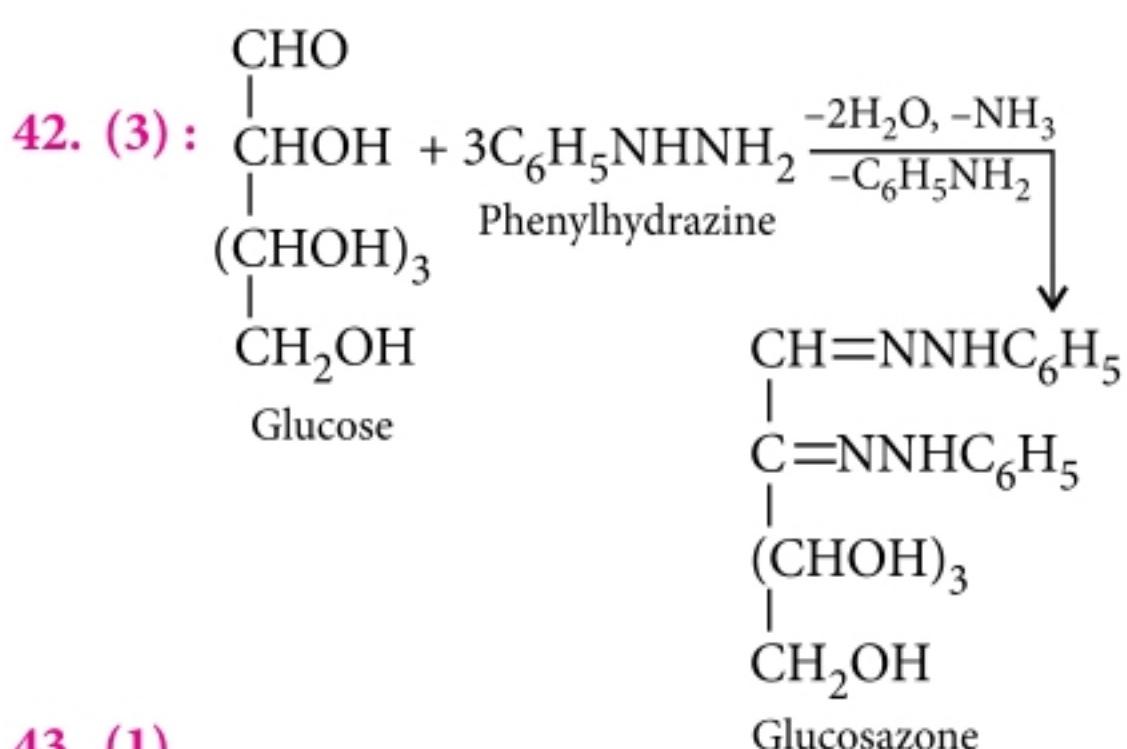
35. (b) : During hydrolysis of proteins we get only α -amino acids.

36. (c) : Gabriel synthesis can be used only for the preparation of primary amines.

37. (c) : Antibodies are proteins which defend the body against the invasion of foreign organisms.

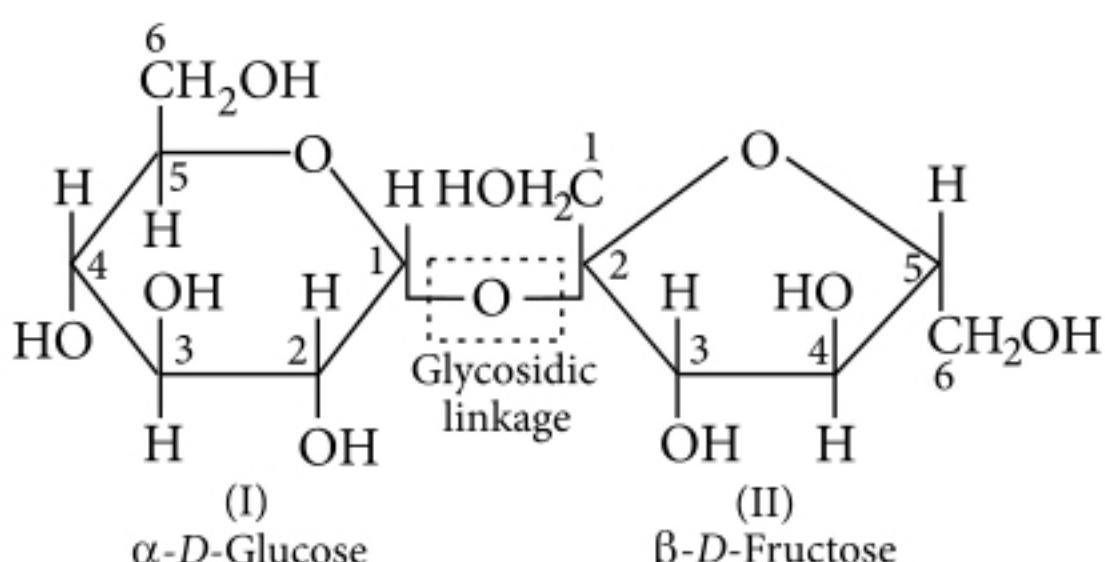
38. (c) 39. (b) 40. (a)

41. (4) : Primary and secondary amines react with CS_2 .

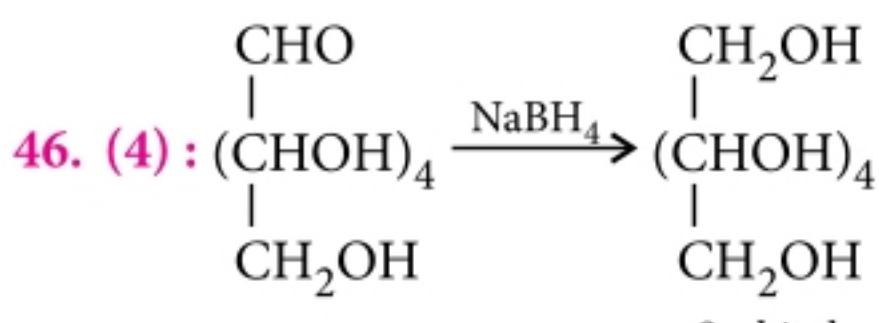


43. (1)

44. (2)



45. (2) : Both aliphatic and aromatic secondary amines undergo Liebermann's nitroso reaction. Thus, this test is used to separate secondary amines from primary and tertiary amines.



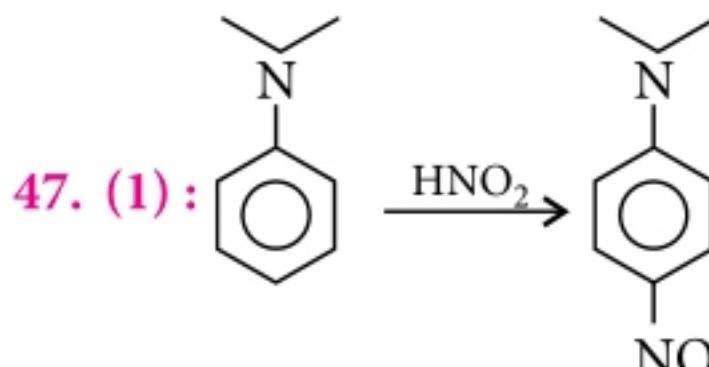
No. of chiral carbon atoms (n) in sorbitol = 4

No. of optical active isomers(a) $\equiv 2^{n-1}$

No. of optical active isomers (n) = 2^{n-1}

No. of racemic forms (r) = $\frac{a}{2} = \frac{b}{2} =$

2 2



48. (1) 49. (3) 50. (2)

SOLUTIONS TO OCTOBER 2014 CROSSWORD

Winners of October 2014 Crossword

Anurag Bera (West Bengal): MTG magazine plays a role of a proper guide in my study. I was totally influenced by this 'Crossword'. It helps to increase anyone's thinking ability and check their subject depth. So, it is a 'fabulous booster' for me as well as all MTG readers.

Aditi Rastogi (Bhopal): The concept of ‘Crossword’ is very good. It helps to revise my concept in chemistry.

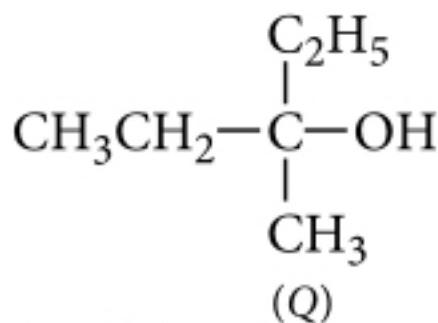
Sender of September 2014 Crossword

Shubham Panwar (Rajasthan)

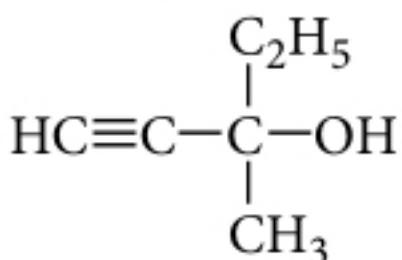
CHEMISTRY MUSING

SOLUTION SET 15

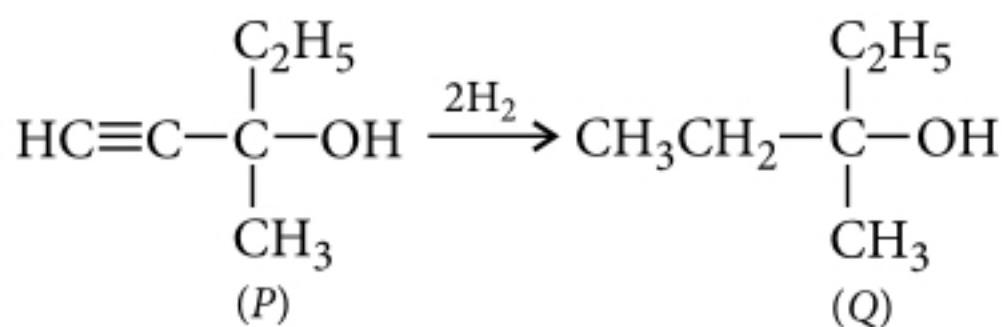
1. (b): Optically active alcohol ($C_6H_{10}O$) is an unsaturated alcohol containing $C\equiv C$ bond, since it absorbs two moles of hydrogen. Compound (Q) being optically inactive must be a tertiary alcohol, since it is resistant to oxidation by CrO_3 . Therefore, its structure should be



and thus (P) is



Hence, the reaction is



2. (c): Perhydrol is 30% H_2O_2 .

Using the relation,

$$\text{Volume strength} = 5.6 \times \text{Normality}$$

$$\begin{aligned} &= 5.6 \times \frac{\text{Percentage strength}}{\text{Eq. wt. of } H_2O_2} \times 10 \\ &= 5.6 \times \frac{30}{17} \times 10 = 98.82 \approx 99 \end{aligned}$$

3. (d): Aspirin being a weak acid remains un-ionised in the stomach (acidic medium) but completely ionised in small intestine (alkaline medium) due to the common ion effect.

4. (c): $P_1 = P$; $V_1 = V$; $P_2 = 2P$; $V_2 = 2V$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{PV}{T_1} = \frac{2P \times 2V}{T_2}$$

$$T_2 = 4T_1$$

P and V remain constant, when air is taken in.

Thus,

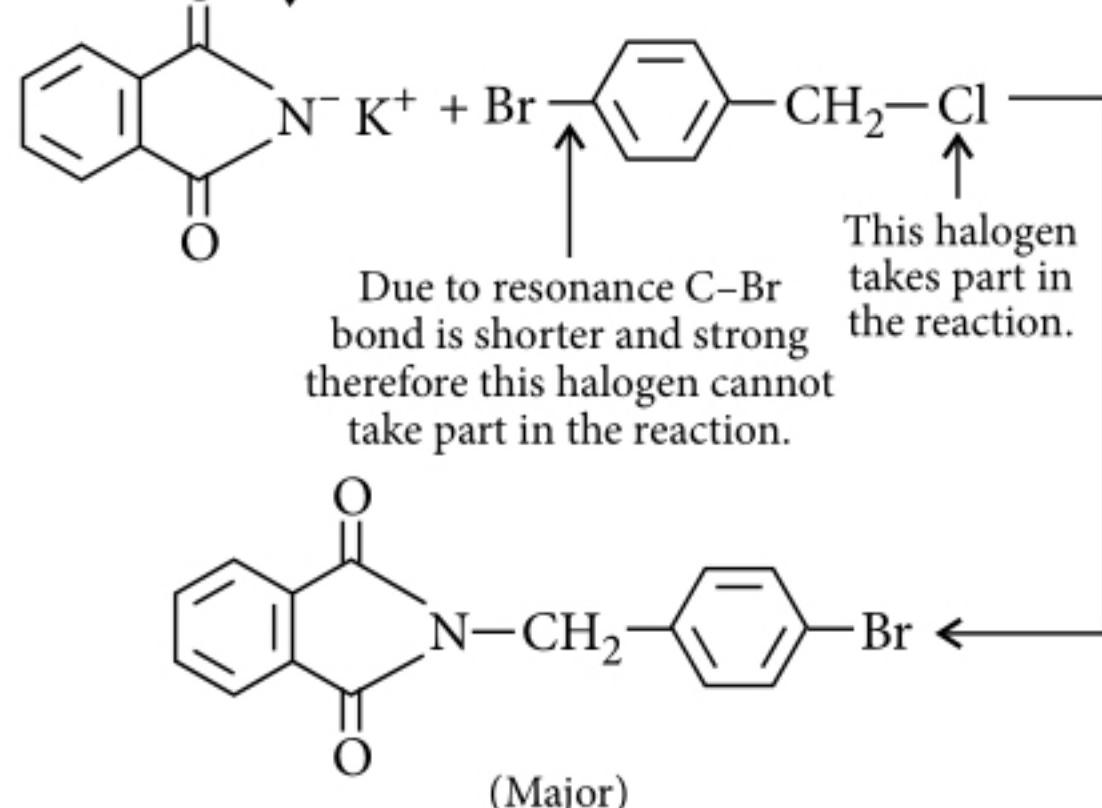
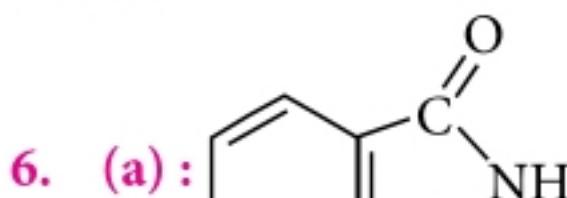
$$n \cdot 4T_1 = n' T'$$

where n and n' are the number of moles at temperatures $4T_1$ and T' respectively.

$$n' = n + \frac{1}{4}n = \frac{5}{4}n$$

$$\therefore n \cdot 4T_1 = \frac{5}{4}n \cdot T' \Rightarrow T' = \frac{16}{5}T_1$$

5. (d)



This halogen takes part in the reaction.

7. (d): Any metal placed below hydrogen in electrochemical series will not give its sulphate with dil. H_2SO_4 .

8. (d): With the exception of Li_2SO_4 , other alkali metal sulphates are water soluble.

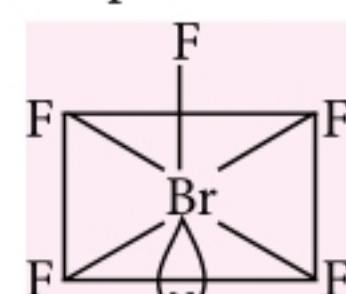
9. (6): 50 mL of 1 M oxalic acid $[(COOH)_2 \cdot 2H_2O]$
 $= 0.050 \text{ mol} = 0.050 \times 126 = 6.3 \text{ g}$

$$\begin{aligned} 50 \text{ mL of } 0.5 \text{ M oxalic acid} &= 6.3 \times 0.5 = 3.15 \text{ g} \\ \therefore \text{Oxalic acid adsorbed on } 0.5 \text{ g wood charcoal} &= 6.3 - 3.15 = 3.15 \text{ g} \end{aligned}$$

$$\begin{aligned} \therefore \text{Amount of oxalic acid adsorbed per gram} \\ \text{of charcoal} &= \frac{3.15}{0.5} = 6.30 \text{ g} \approx 6.0 \text{ g} \end{aligned}$$

10. (8): BrF_5 is square pyramidal in shape.

The observed bond angles are 87° , which is close to the theoretical 90° . This slight distortion is caused due to presence of one lone pair of electrons on Br -atom.



Chemistry Olympiad

1. When *threo*-3-bromo-2-butanol is hydrolysed with $\text{NaOH}_{(aq)}$ the product obtained is
 - (a) *erythro*-3-bromo-2-butanol
 - (b) *threo*-2,3-dihydroxybutane
 - (c) optically active 2,3-dihydroxybutane
 - (d) *meso*-2,3-butanediol.
2. The pH of D_2O and H_2O at 298 K is
 - (a) 7.43 and 7.0
 - (b) 7.0 and 7.0
 - (c) 7.0 and 6.85
 - (d) 6.85 and 7.35
3. During the adsorption of krypton on activated charcoal at low temperature
 - (a) $\Delta H < 0$ and $\Delta S < 0$
 - (b) $\Delta H > 0$ and $\Delta S < 0$
 - (c) $\Delta H > 0$ and $\Delta S > 0$
 - (d) $\Delta H < 0$ and $\Delta S > 0$
4. Oil spreads on water surface because
 - (a) oil is denser than water
 - (b) surface tension of oil is more than water
 - (c) surface tension of oil is less than water
 - (d) none of the above.
5. Which one undergoes facile decarboxylation?
 - (a) $\text{H}_2\text{C}\begin{cases} \text{COOC}_2\text{H}_5 \\ \text{COOC}_2\text{H}_5 \end{cases}$
 - (b) $\text{Ph}-\text{CH(OH)}-\text{COOH}$
 - (c) $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{CH(OH)}-\text{CH}_3$
 - (d) $\text{C}_6\text{H}_5-\text{COCH}_2-\text{COOH}$
6. If two compounds have the same empirical formula but different molecular formula, they must have
 - (a) different percentage composition
 - (b) different molecular weights
 - (c) same viscosity
 - (d) same vapour pressure.
7. In Ramsay and Rayleigh's isolation of noble gases from air, the nitrogen of the air is finally converted into
 - (a) NaNO_2 only
 - (b) NO and NO_2
 - (c) NaNO_3 only
 - (d) NaNO_2 and NaNO_3
8. Two oxides of an element contain 57.1% and 72.7% of oxygen. If the first oxide is MO then second oxide is
 - (a) MO
 - (b) M_2O
 - (c) MO_3
 - (d) MO_2
9. The inversion of table sugar (sucrose) in acidic medium proceeds with a half-life 450 minute at $\text{pH} = 5$ for any concentration of table sugar. The half-life changes to 45 minutes if $\text{pH} = 6$, the inversion of table sugar follows the rate law expression
 - (a) $r = k[\text{sugar}]^1[\text{H}^+]^0$
 - (b) $r = k[\text{sugar}]^1[\text{H}^+]^1$
 - (c) $r = k[\text{sugar}]^0[\text{H}^+]^1$
 - (d) $r = k[\text{sugar}]^2[\text{H}^+]^0$
10. The position of equilibrium lies to the right in each of these reactions.

$$\text{N}_2\text{H}_5^+ + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{N}_2\text{H}_4$$

$$\text{NH}_3 + \text{HBr} \rightleftharpoons \text{NH}_4^+ + \text{Br}^-$$

$$\text{N}_2\text{H}_4 + \text{HBr} \rightleftharpoons \text{N}_2\text{H}_5^+ + \text{Br}^-$$

Based on this information, what is the order of acidic strength?

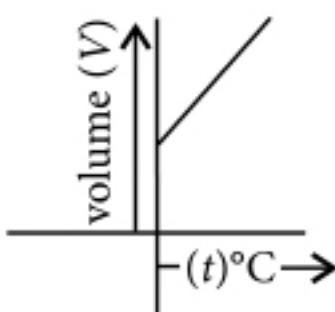
 - (a) $\text{HBr} > \text{N}_2\text{H}_5^+ > \text{NH}_4^+$
 - (b) $\text{N}_2\text{H}_5^+ > \text{N}_2\text{H}_4 > \text{NH}_4^+$
 - (c) $\text{NH}_3 > \text{N}_2\text{H}_4 > \text{Br}^-$
 - (d) $\text{N}_2\text{H}_5^+ > \text{HBr} > \text{NH}_4^+$

- 11.** When a Cu-Zn galvanic cell operates under standard conditions,
- the concentration of Zn^{2+} ions in the zinc half-cell gradually decreases
 - the concentration of Cu^{2+} ions in the copper half-cell gradually increases
 - negative ions migrate from the zinc half-cell to the copper half-cell
 - the intensity of the colour of the electrolyte in the copper half-cell gradually decreases.

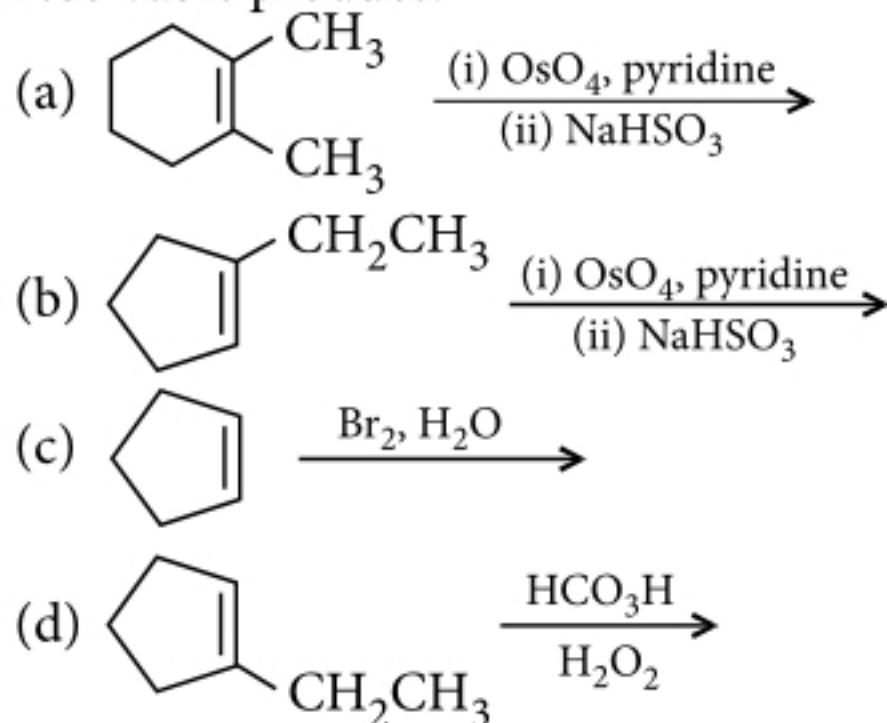
- 12.** According to Charles' law, volume of a gas can be plotted against temperature in celsius as shown in the graph.

If V_0 is the volume of a gas at $0^\circ C$ and V_t is the volume at $t^\circ C$ then slope of the straight line is equal to

- $\frac{V_0}{273}$
- $\frac{1}{273}$
- $\frac{V_t}{273}$
- V_0



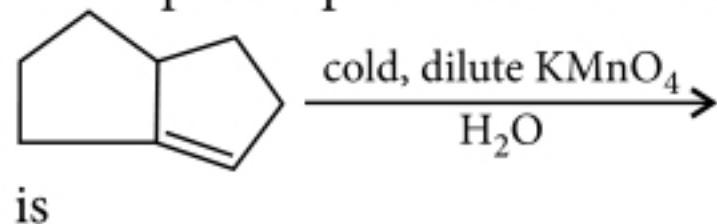
- 13.** Which of the following reactions gives non-resolvable product?



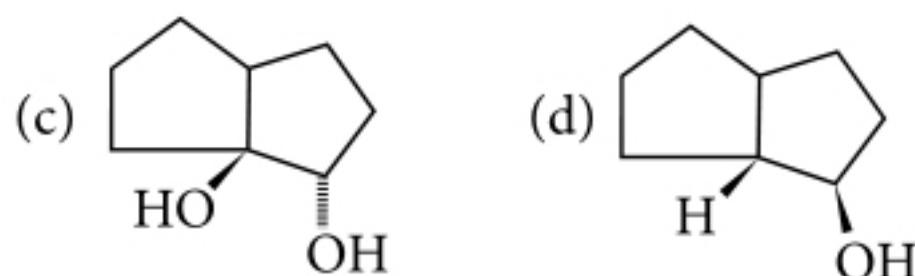
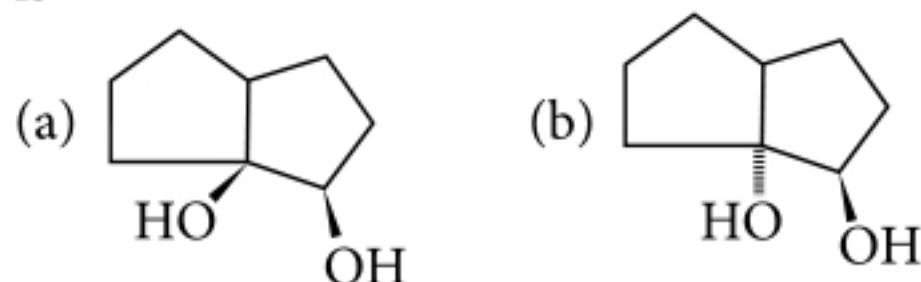
- 14.** Which one of the following is a covalent crystal?

- Rock salt
- Ice
- Quartz
- Dry ice

- 15.** The expected product in the reaction,

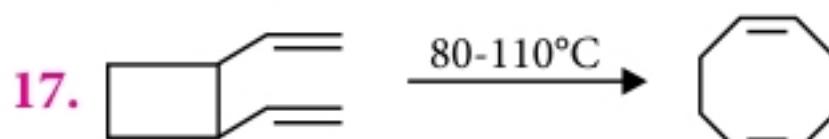


is



- 16.** An alloy of Cu, Au and Ag is found to have Cu constituting the *ccp* lattice. If Ag atoms occupy the edge centres and Au is present at body centre, the alloy has formula

- Cu_4Ag_2Au
- Cu_4Ag_4Au
- Cu_4Ag_3Au
- $CuAgAu$



Transition state in this transformation is

- chair
- boat
- half chair
- no transition state due to fast rupture of bonds.

- 18.** The critical micelle concentration (CMC) is

- the concentration at which micellization starts
- the concentration at which the true solution is formed
- the concentration at which one molar electrolyte is present per 1000 g of the solution
- the concentration at which $\Delta H = 0$

- 19.** Least energetic conformation of cyclohexane is

- chair conformation
- boat conformation
- half-chair conformation
- twist-boat conformation.

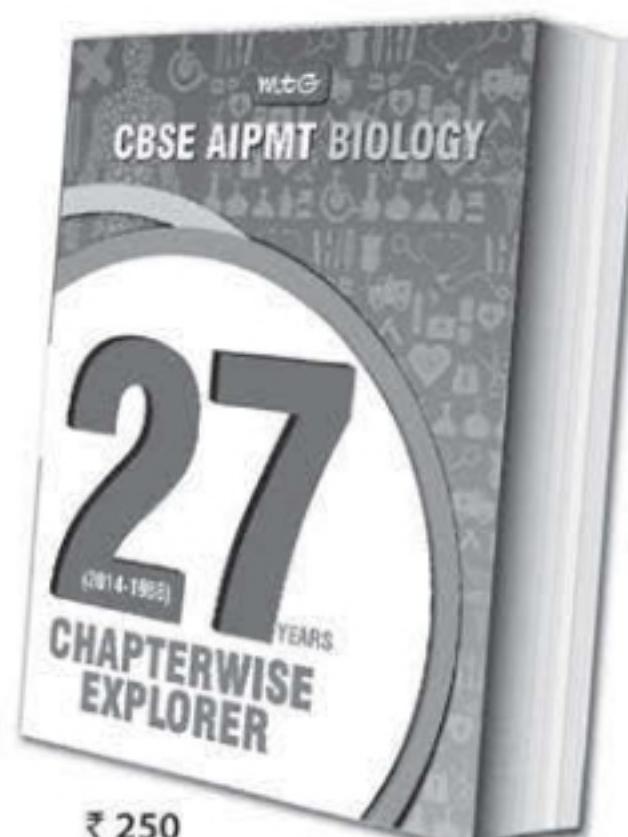
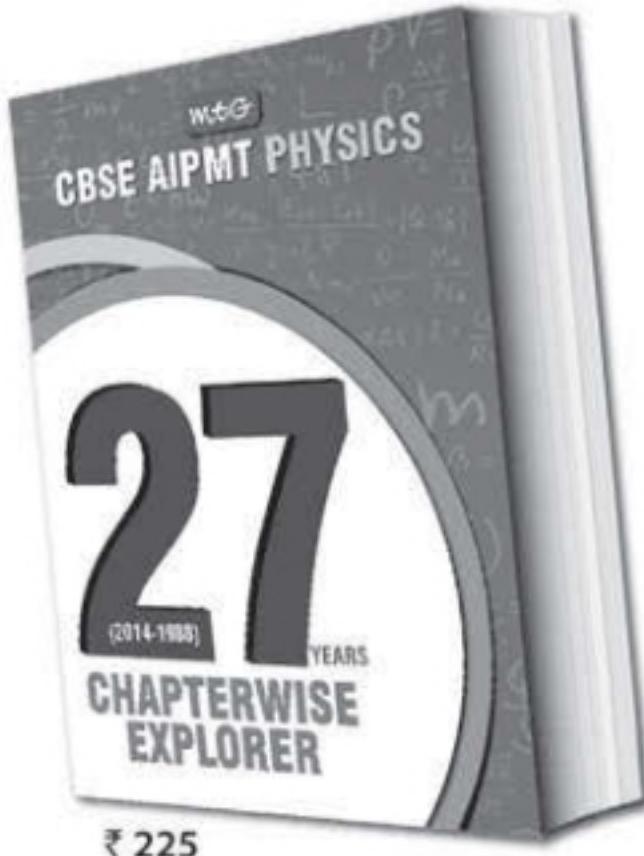
- 20.** Nylon is used in many things in our today's life, like umbrellas, tyre cords and brushes, etc. Which of the following has the same linkage as nylon?

- Vitamins
- Fats
- Proteins
- Carbohydrates

- 21.** The reaction of benzene with *iso*-butene in the presence of sulphuric acid gives

- iso*-butylbenzene
- tert*-butylbenzene
- n*-butylbenzene
- no reaction.

The most comprehensive question bank books that you cannot afford to ignore



27 Years' Physics, Chemistry & Biology contain not only chapter-wise questions that have appeared over the last 27 years in CBSE's PMT, but also full solutions, that too by experts. Needless to say, these question banks are essential for any student to compete successfully in AIPMT. More so since almost 50% of questions in AIPMT are from previous years.

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- Chapterwise segregation of questions to help you assess the level of effort required to succeed
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- 22.** The molar enthalpy of fusion of water is 6.01 kJ mol^{-1} . The entropy change of 1 mole of ice at its melting point will be
 (a) $22 \text{ J K}^{-1} \text{ mol}^{-1}$ (b) $109 \text{ J K}^{-1} \text{ mol}^{-1}$
 (c) $44 \text{ J K}^{-1} \text{ mol}^{-1}$ (d) $11 \text{ J K}^{-1} \text{ mol}^{-1}$
- 23.** Which of the following is most likely structure of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, if $1/3$ of total chlorine of the compound is precipitated by adding AgNO_3 to its aqueous solution?
 (a) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$
 (b) $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3](\text{H}_2\text{O})_3$
 (c) $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$
 (d) $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$
- 24.** NaCl shows Schottky defects and AgCl Frenkel defects. Their electrical conductivity is due to the
 (a) motion of ions and not the motion of electrons
 (b) motion of electrons and not the motion of ions
 (c) lower coordination number of NaCl
 (d) higher coordination number of AgCl .
- 25.** The concentration of B at the point of intersection of the two curves as shown in the figure for, $A \rightarrow nB$, is
 (a) $\frac{nC_0}{2}$ (b) $\frac{nC_0}{n-1}$
 (c) $\frac{nC_0}{n+1}$ (d) $\left(\frac{n-1}{n+1}\right)C_0$
- 26.** A reaction having equal energies of activation for forward and reverse reactions has
-
- (a) $\Delta H = 0$ (b) $\Delta H = \Delta G = \Delta S = 0$
 (c) $\Delta S = 0$ (d) $\Delta G = 0$
- 27.** The addition of KI increases the rate of the reaction,
 $\text{CH}_3\text{CH}_2\text{Cl} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{HCl}$
 This is because I^- is
 (a) a good nucleophile and a good leaving group
 (b) a poor nucleophile and a poor leaving group
 (c) a poor nucleophile and a good leaving group
 (d) none of the above.
- 28.** Temperature coefficient of a reaction is '2'. When temperature is increased from 30°C to 90°C , the rate of reaction is increased by
 (a) 60 times (b) 64 times
 (c) 150 times (d) 400 times.
- 29.** Rice is deficient in
 (a) alanine (b) glycine
 (c) lysine (d) leucine.
- 30.** The ozonolysis of benzene produces
 (a) glyoxal (b) ethylglyoxal
 (c) dimethylglyoxal (d) methylglyoxal.

ANSWER KEY

- | | | | | |
|----------------|----------------|----------------|----------------|----------------|
| 1. (d) | 2. (a) | 3. (a) | 4. (c) | 5. (d) |
| 6. (b) | 7. (d) | 8. (d) | 9. (a) | 10. (a) |
| 11. (d) | 12. (a) | 13. (a) | 14. (c) | 15. (a) |
| 16. (c) | 17. (b) | 18. (a) | 19. (a) | 20. (c) |
| 21. (b) | 22. (a) | 23. (c) | 24. (a) | 25. (c) |
| 26. (a) | 27. (a) | 28. (b) | 29. (c) | 30. (a) |

OO

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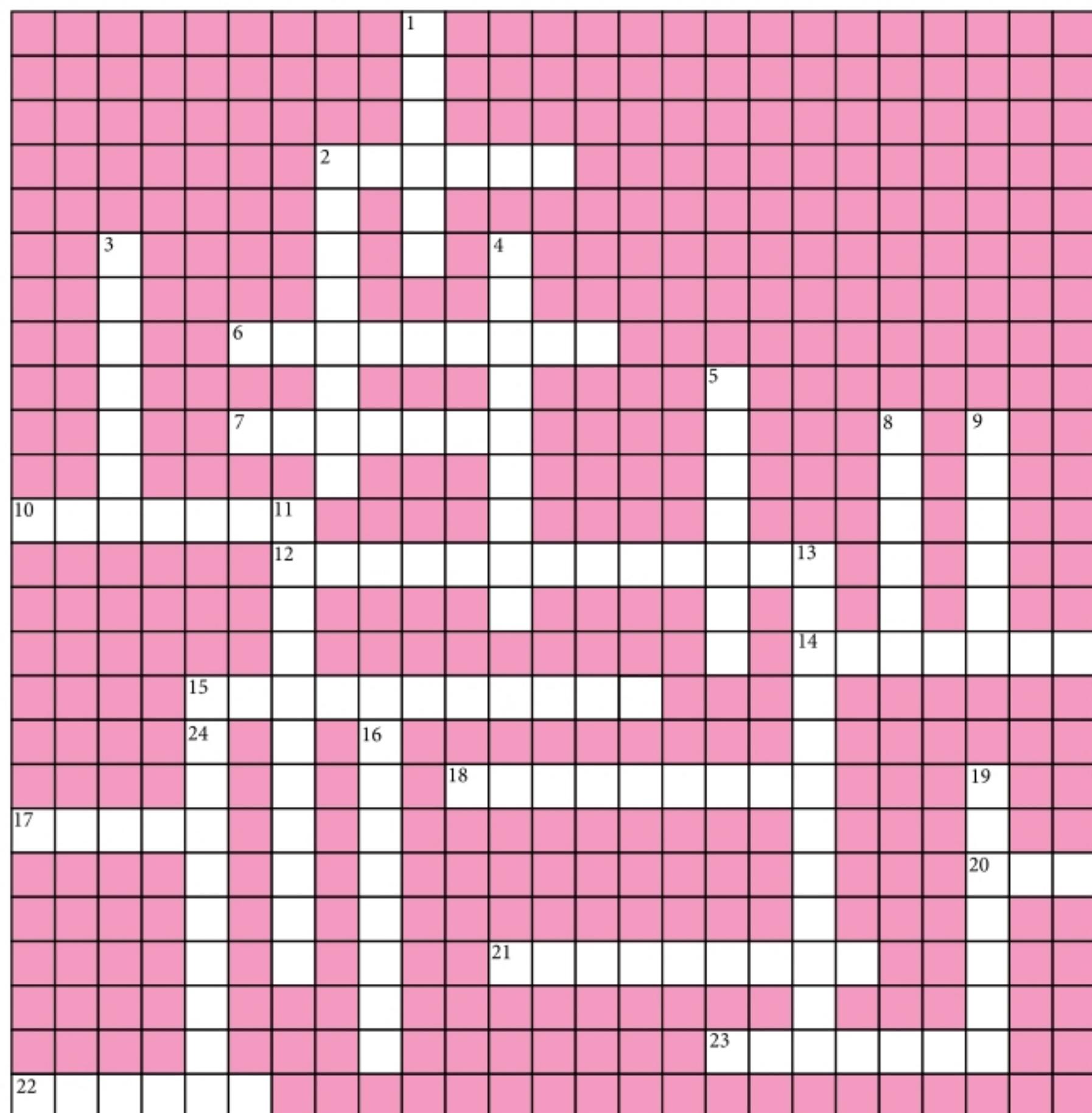
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CROSSWORD

Readers can send their answer to win exciting prizes. Winners' name with their valuable feedback will be published in next issue.

ACROSS

2. Glass used for making lenses. (6)
6. Effect develops between a π -bond and a lone pair. (9)
7. Effect, due to scattering of light but not observed in sugar solution. (7)
10. Name of the ion $\text{C}_2\text{H}_3\text{O}_2^-$. (7)
12. A catalyst used for contact process (metal in + 5 O.S.). (13)
14. Pure substance containing only one type of atoms. (7)
15. Doeblin modification of aldol condensation. (11)
17. BH_3 exists as (5)
18. Common name for $\text{Ca}(\text{OH})_2$. (9)
20. The no. of C-atoms in dibromomethane. (3)
21. A chemical used in cleaning products, which is environmentally unfriendly. (9)
22. He gave the first insight into the structure of benzene. (6)
23. Sugar, which gives β -D-glucose and β -D-galactose on hydrolysis. (7)



DOWN

1. If the carbonyl group is not at the end of a carbon chain, the substance is. (6)
2. A pyrimidine base present in DNA. (8)
3. Reaction intermediate formed in Reimer-Tiemann reaction. (7)

4. An alloy, used in aircraft industry for its light weight. (9)
5. The reaction in which the final product obtained is β -amino-carbonyl compound. (7)
8. The flame colour for potassium, a bit like lilac too. (6)
9. A torch to caramelize sugar in cooking. (6)
11. Change from a liquid to a gas. (11)
13. Electrolytes are _____ conductors. (12)
16. Electrons float around the atom in distinct shell-like arrangements called. (8)
19. Highly vulcanized rubber containing 20-30% sulphur. (7)
24. 30% H_2O_2 . (9)



YOU ASKED WE ANSWERED

Do you have a question that you just can't get answered?

Use the vast expertise of our mtg team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough.

The best questions and their solutions will be printed in this column each month.

Q1. In organic chemistry, what is the actual difference between aqueous KOH and alcoholic KOH as reagent?

– Ratnadeep Das, Silchar, Assam

OR

What is the use of aqueous KOH in organic reactions?

– Sachin Dhiman

Ans. Type of reaction, depends upon the nature of reagent used.

1. The solvent

The proportion of water to ethanol in the solvent matters.

- Water $\xrightarrow{\text{Encourages}}$ Substitution reaction.
- Ethanol $\xrightarrow{\text{Encourages}}$ Elimination reaction.

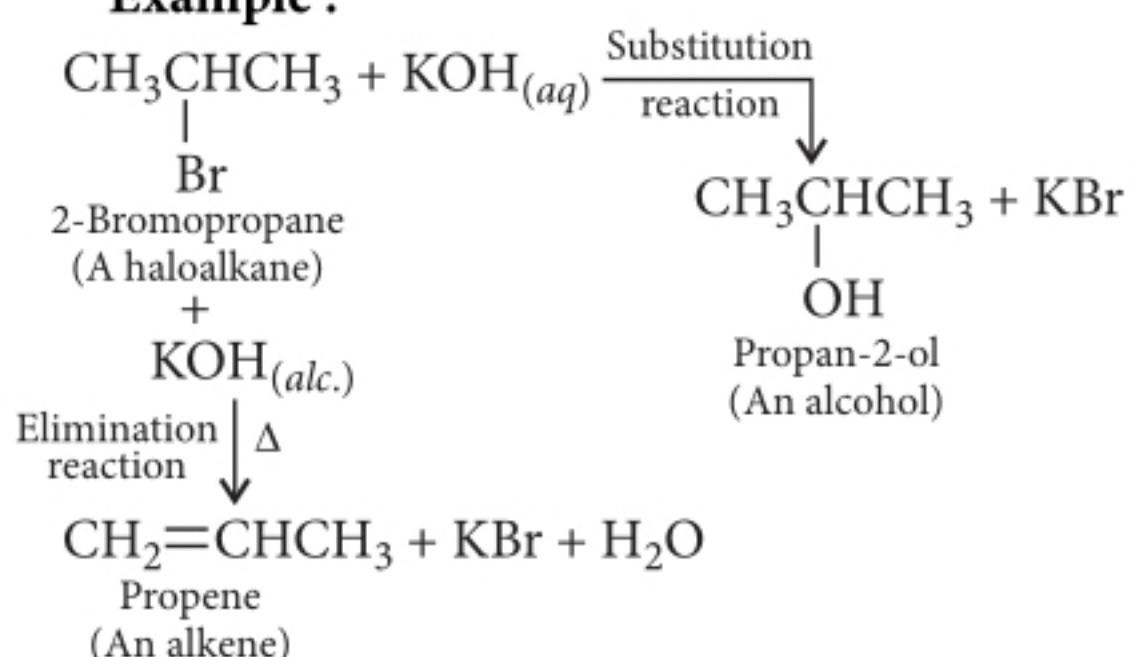
2. The temperature

- Higher temperature $\xrightarrow{\text{Encourages}}$ Elimination reaction.

3. The concentration of KOH solution

- Higher concentration $\xrightarrow{\text{Favours}}$ Elimination reaction.

Example :



Q2. Why chemical formula of water is represented as H₂O not OH₂ and ammonia as NH₃ not H₃N?

– Mohd. T. Khan and Arun Nayan, Ghazipur, U.P.

Ans. Covalent compounds (or, molecular compounds) are formed between non-metals only. Some compounds are identified with their unique names and formulae. For compounds, water and ammonia, the empirical formula is same as the molecular formula.

Compound	Proper name	Empirical formula	Molecular formula
Water	Dihydrogen oxide	H ₂ O	H ₂ O
Ammonia	Nitrogen trihydride	NH ₃	NH ₃

Hence, they can be represented as H₂O and NH₃.

Q3. Why the elements having d¹⁰ configuration are not considered as ‘transition elements’?

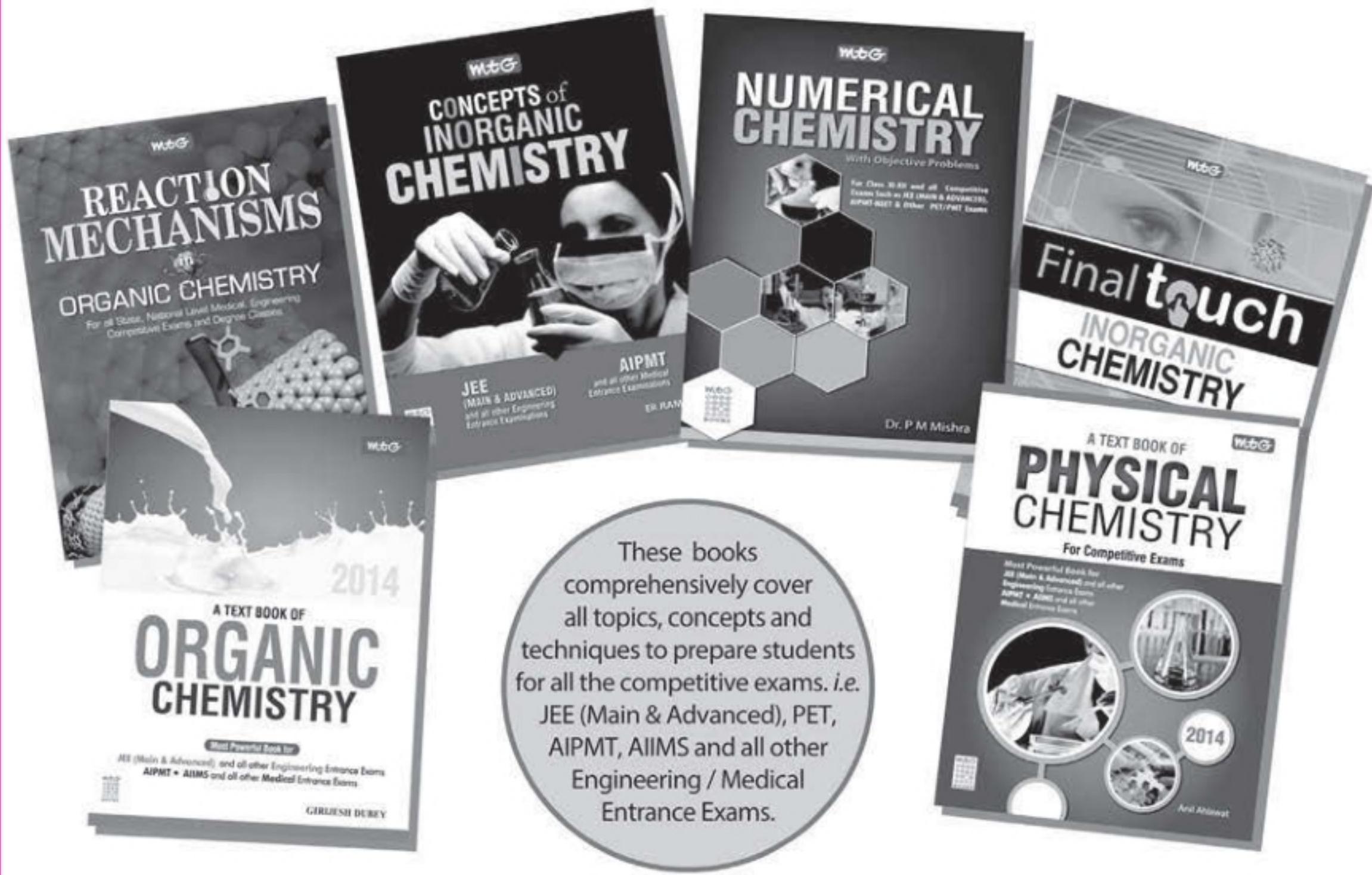
– Chirag Thakar

Ans. The modern, IUPAC definition states that a transition metal is “an element whose atom has an incomplete d-subshell, or which can give rise to cations with an incomplete d-subshell”.

- The elements of group 12 (Zn, Cd and Hg) have a completely filled (n – 1)d-subshell in their elementary form as well as in the combined state (M²⁺ ions). These elements do not show much resemblance with other d-block elements except for their ability to form complexes.
- Apart from this, elements of group 3 (Sc, Y, La and Ac) form ions by losing three outer electrons and end up with noble gas configuration. Hence, these elements also do not meet the definition. However, they are d-block elements.



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SUPER-ZOOM MICROSCOPE : WON THE CHEMISTRY NOBEL PRIZE 2014

Year 2014 is remarkable for Chemistry. Three scientists Eric Betzig, William Moerner (Americans) and Stefan Hell (German) won the Nobel Prize in Chemistry on 8th October for developing new methods that let microscopes see finer details than they could before.

Dr. Betzig, a group leader at the Janelia Research Campus works to develop novel optical imaging tools to open new windows into molecular, cellular and neurobiology. Dr. Moerner, a professor at Stanford University works in the field of single – molecule spectroscopy, super resolution imaging, and trapping of single biomolecules and photosynthetic proteins. Dr. Hell, one of the directors at the Max Planck Institute for Biophysical Chemistry in Goettingen works in the field of Far-Field Optical Nanoscopy.

Importance of Optical Microscopy

Optical microscopy has always played a prominent role in many scientific fields, especially in life sciences. This is based on rather exclusive advantages such as noninvasive access to the interior of (living) cells and specific and highly sensitive detection of cellular constituents through fluorescent tagging. These advantages always remained the major drawback for electron and scanning probe microscopy - although providing nanoscale resolution down to the atomic level they cannot make up with the inherent incompatibility with living matter.

Until the mid of the 1990s, obtaining a resolution on the nanometer scale with focused visible light was considered unfeasible because due to diffraction a focal spot is limited in its width to about half the wavelength of the used light. Only in recent years methods to surpass the diffraction barrier have been invented making the major disadvantage of optical microscopy obsolete. Optical imaging with subdiffraction resolution has an impact on numerous fields of research including cell biology, medicine or material science.



Eric Betzig

W.E. Moerner

Stefan W. Hell

Success Journey : Research to Nobel

- Their breakthroughs, starting in the 1990s, shattered previous limits on the resolution of optical microscopes, giving scientists improved tools to study diseases such as Parkinson's, Alzheimer's and Huntington's at a molecular level.
- Hell has peered inside living nerve cells in order to better understand brain synapses. Moerner studied proteins in relation to Huntington's disease. Betzig's work is the study of cell division inside the embryos.
- Prof. Hell developed the stimulated emission depletion (sted) microscopy in 2000. The other method, single molecule microscopy was developed separately by Prof. Betzig and Prof. Moerner.

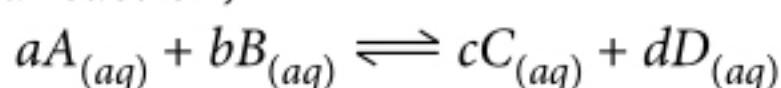
Significance

- The Nobel committee says the work "has brought optical microscopy into the nano-dimension."
- The path of the individual molecules inside the living cells gave different colours after irradiation, characteristic of the molecules which has led to a revolution in the field of microscopy all over the world.



Equilibrium

- In physical equilibrium, opposing processes involve physical changes.
- In chemical equilibrium, opposing processes involve chemical changes.
- **Chemical equilibrium** may be defined as the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentrations of reactants and products do not change with time.
- At equilibrium, both reactions *i.e.* forward and backward continue to perform and such a state of equilibrium where both opposing forces balance each other and molecular activity still continues is known as **dynamic equilibrium**.
- At equilibrium, the **Gibb's free energy** (G) is minimum and no change taking place at equilibrium proceeds without change in free energy *i.e.* $\Delta G = 0$.
- According to **law of mass action**, the rate of a chemical reaction is proportional to the product of the active masses of the reactants.
- Chemical equilibrium at a given temperature is characterised by constancy of certain observable properties such as pressure, concentration, density or colour.
- A **catalyst** can hasten the approach of equilibrium but does not alter the state of equilibrium.
- For a reaction,

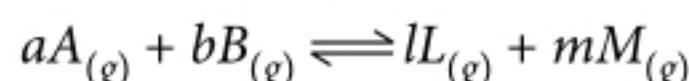


$$\frac{k_1}{k_2} = K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where K_c is known as the equilibrium constant. This is called **law of chemical equilibrium**.

- **Equilibrium constant** K_c is simply the ratio of the rate constants of two opposing reactions and it is constant as a given temperature.

- For a general gaseous reaction:



the equilibrium constant K_p is given by

$$K_p = \frac{[P_L]^l [P_M]^m}{[P_A]^a [P_B]^b}$$

i.e. partial pressure is taken in place of molar concentration.

- Equilibrium constants K_p and K_c are related as

$$K_p = K_c (RT)^{\Delta n_g}$$

where Δn_g is the difference of the sum of the coefficients for the gaseous products and reactants. If $\Delta n_g = 0$, $K_p = K_c$. If $\Delta n_g = +ve$, $K_p > K_c$. If $\Delta n_g = -ve$, $K_p < K_c$

- If reaction is reversed, equilibrium constant is inverted. *i.e.*, $K' = 1/K$.
- If equation for a reaction is divided by a factor of ' n ', the new equilibrium constant becomes n^{th} root of the previous equilibrium constant.

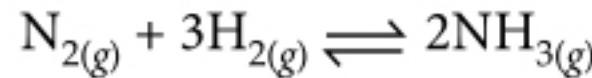
$$\text{i.e., } K' = \sqrt[n]{K}$$

- If equation for a reaction is multiplied by a factor ' n ' then the new equilibrium constant (K') becomes equal to K^n . *i.e.*, $K' = K^n$

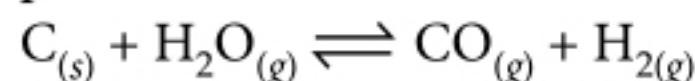
- If equation is written in a number of steps, then its equilibrium constant will be multiple of equilibrium constants of each step.

$$\text{i.e., } K = K_1 \times K_2 \times K_3 \times \dots K_n$$

- In **homogeneous equilibrium**, all the reactants and products are in the same phase.



- In **heterogeneous equilibrium**, the reactants and products are present in two or more phases.



- Predicting the extent of reaction:

- $K_c > 10^3$ [Forward reaction is favoured.]

- $K_c < 10^{-3}$ [Reverse reaction is favoured.]
- $10^{-3} < K_c < 10^3$ [Both reactants and products are present in equilibrium.]
- Predicting the direction of reaction:
 - $Q_c > K_c$ [Reverse reaction is favoured.]
 - $Q_c < K_c$ [Forward reaction is favoured.]
 - $Q_c = K_c$ [Reaction is in equilibrium.]
- **van't Hoff's isotherm** is given by the equation

$$\Delta G = \Delta G^\circ + RT \ln J$$

where ΔG° is the free energy change of the reaction when the products and the reactants are all in their respective standard states and J stands for the reaction coefficient of partial pressures of the products and reactants.
- At equilibrium,

$$\Delta G^\circ = -RT \ln K; K = e^{-\Delta G^\circ/RT}$$
 - If $\Delta G^\circ < 0$ then $K > 1$
[Forward reaction is favoured.]
 - If $\Delta G^\circ > 0$ then $K < 1$
[Reversed reaction is favoured.]
 - If $\Delta G^\circ = 0$, then $K = 1$
[Reaction is in equilibrium.]
- $$\frac{d \ln K_p}{dt} = \frac{\Delta H^\circ}{RT^2}$$
 is known as **van't Hoff's equation**.

where ΔH° is the standard enthalpy change for the reaction at constant pressure when the reactants as well as the products are in their standard states.
- $$\log \frac{K''_p}{K'_p} = \frac{\Delta H^\circ}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

where K''_p is the equilibrium constant at temperature T_2 , K'_p is the equilibrium constant at temperature T_1 and ΔH is heat of reaction (enthalpy change).
- According to **Le-Chatelier's principle**, if a system in equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effects of the change imposed.
- **Change in concentration** : Increasing the concentrations of the reactants results in shifting the equilibrium in favour of the products while increasing the concentration of the products results in shifting the equilibrium in favour of the reactants.

- **Change in pressure** : The increase of pressure on a chemical equilibrium shifts it in that direction in which the number of molecules decreases and vice-versa.
- **Change in temperature** : The increase of temperature favours the reverse change in an exothermic reaction and the forward change in an endothermic reaction.
- **Effect of adding inert gas** : Addition of inert gas at constant volume does not affect the equilibrium and addition of inert gas at constant pressure favours the direction in which larger number of moles of the gas are produced.
- **Effect of adding catalyst** : The addition of catalyst does not affect the equilibrium.
- **Ionic equilibrium** is the study of equilibrium in the reactions where formation of ions take place in aqueous solution.
- **Ionisation of acids**:

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

As K_a increases, pK_a decreases and acidity increases.
- **Ionisation of bases**:

$$BOH_{(aq)} \rightleftharpoons B^+_{(aq)} + OH^-_{(aq)}$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$pK_b = -\log K_b$$

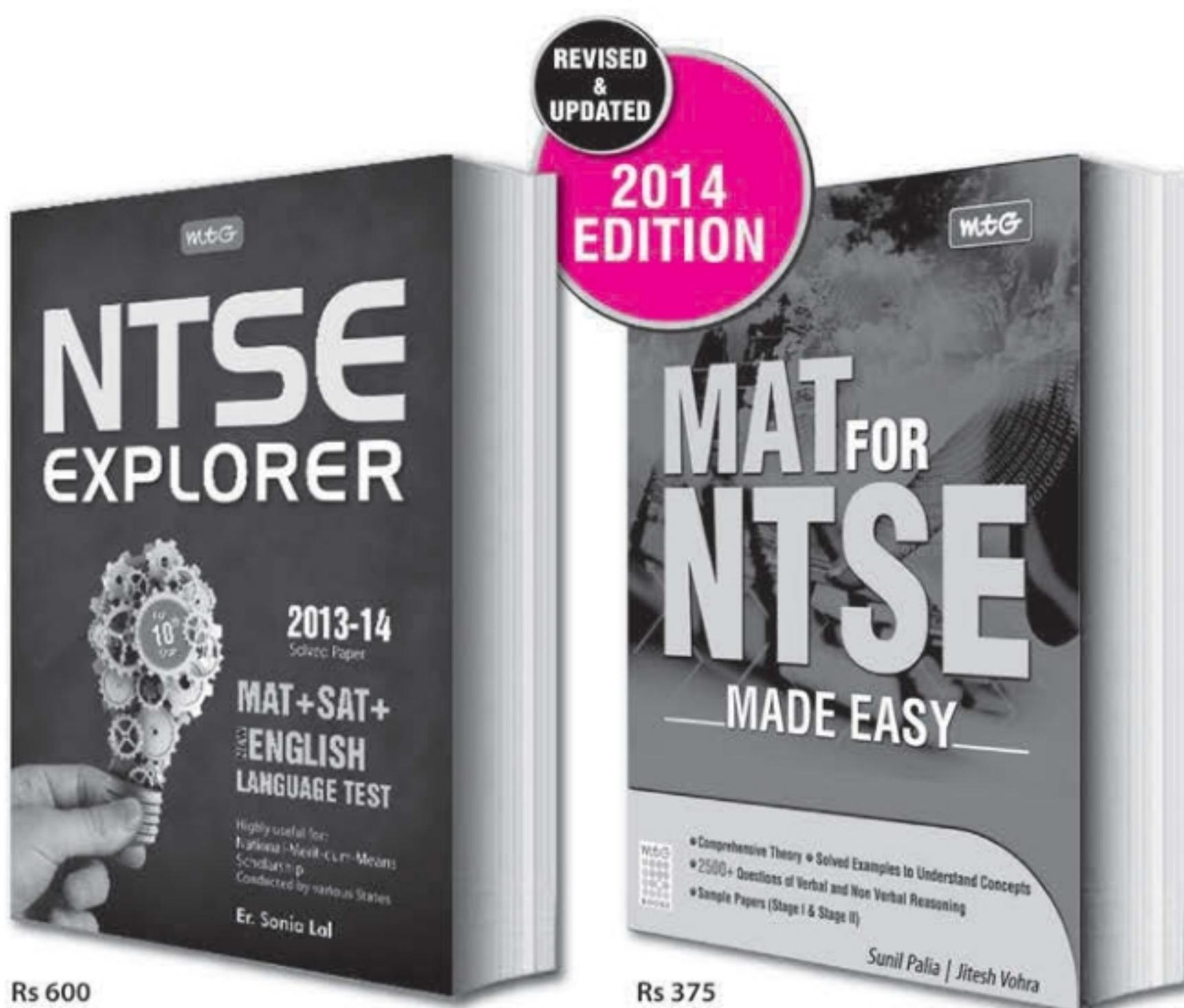
As K_b increases, pK_b decreases and basicity increases.
- **Multistage ionisation of acids and bases**
 For a polybasic acid,

$$K_{a1} > K_{a2} > K_{a3}$$
 and so on.
 For a polyacidic base,

$$K_{b1} > K_{b2} > K_{b3}$$
 and so on.
- According to **Arrhenius theory**, an acid is a compound that releases H^+ ions in water and base is a compound that releases OH^- ions in water.
- According to **Bronsted-Lowry concept**, an acid is any molecule or ion that can donate a proton (H^+) and base is any molecule or ion that can accept a proton.

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- The strength of a Bronsted acid depends upon its tendency to donate a proton. The strength of a Bronsted base depends upon its ability to accept a proton.
- Some common acids have been arranged in the following order of their acid strengths : $\text{HClO}_4 > \text{HBr} > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$
- The acid (HA) and its conjugate base (A^-) that are related to each other by donating and accepting a single proton are said to constitute a **conjugate acid-base pair**.
- A weak base has strong conjugate acid and a weak acid has a strong conjugate base.
- A strong acid has a weak conjugate base and a strong base has a weak conjugate acid.
- Monoprotic acids** are capable of donating one proton and **monoprotic bases** can accept one proton.
- Polyprotic acids** are capable of donating two or more protons and **polyprotic bases** can accept two or more protons.
- Molecules or ions that can behave both as Bronsted acid and base are called **amphiprotic substances**.
- According to **Lewis concept**, an acid is an electron pair acceptor and base is an electron pair donor.
- According to Ostwald's dilution law for weak electrolytes the degree of dissociation is inversely proportional to the square root of concentration.

$$\alpha \propto \frac{1}{\sqrt{C}} \text{ or, } \alpha = \sqrt{\frac{K_a}{C}}$$

- For two weak acids of dissociation constant K_{a_1} and K_{a_2} at the same concentration,

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} \quad \left[\because \alpha = \sqrt{\frac{K_a}{C}} \right]$$

where α_1 and α_2 are the respective degrees of dissociation of the two acids.

- Degree of dissociation** of an acid is a measure of its capacity to furnish hydrogen ions and hence a measure of its strength.

$$\frac{\text{Strength of one acid, HA}_1}{\text{Strength of another acid, HA}_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Thus, relative strengths of any two weak acids at the same concentration are given by the ratio of the square roots of their dissociation constants.

- The **hydrogen ion concentration** in a solution of a weak acid in water at a given concentration is directly proportional to the square root of the dissociation constant of the acid.

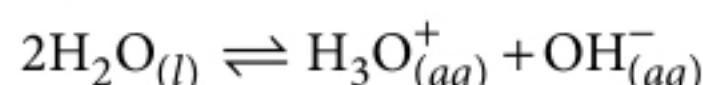
$$[\text{H}^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{CK_a}$$

- The dissociation constant K_b of the base is given by

$$K_b = C\alpha^2 \text{ or, } \alpha = \sqrt{\frac{K_b}{C}}$$

$$\text{or } [\text{OH}^-] = C\alpha = C\sqrt{\frac{K_b}{C}} = \sqrt{CK_b}$$

- Ionic product of water:**



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ M}^2$$

$$\therefore [\text{OH}^-] = [\text{H}^+] = 1.0 \times 10^{-7} \text{ M at } 298 \text{ K}$$

- The **pH of a solution** is the negative logarithm of the concentration (in moles per litre) of hydrogen ions which it contains.
 $\text{pH} = -\log[\text{H}^+]$ or $\text{pH} = -\log[\text{H}_3\text{O}^+]$
 Similarly, negative logarithm of hydroxyl ion concentration is called pOH.
 $\text{pOH} = -\log[\text{OH}^-]$

Relationship between pH and pOH

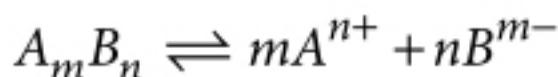
$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} + \text{pOH} = \text{p}K_w$$

$$\text{p}K_a + \text{p}K_b = \text{p}K_w$$

- The scale on which pH values are computed is called the **pH scale**.
- The lower the pH, higher is the $[\text{H}^+]$ or acidity.
- If pH value of a solution is 7, it is **neutral**, if pH value is less than 7, the solution is **acidic** and if it is more than 7, the solution is **alkaline**.
- The **solubility** (S) of a substance in a solvent is the concentration in the saturated solution.
- Molar solubility** is defined as the number of moles of the substance per litre of the solution.

○ **Solubility product :**



$$K_{sp} = [A^{n+}]^m[B^{m-}]^n$$

- $K_{ip} > K_{sp}$, precipitation occurs.
- $K_{ip} < K_{sp}$, precipitation does not occur.
- $K_{ip} = K_{sp}$, solution is saturated.

○ **Relation between solubility and solubility product :**

$$K_{sp} = [mS]^m[nS]^n = m^m S^m \cdot n^n S^n$$

$$= m^m \cdot n^n \cdot (S)^{m+n} \quad [\text{where } S \text{ is solubility.}]$$

- The suppression of the dissociation of a weak acid or a weak base on the addition of an electrolyte containing its own ion is called **common ion effect**.
- A **buffer solution** is one which can resist change in its pH value on the addition of an acid or base.
- The capacity of a solution to resist alteration in its pH value is known as its **buffer capacity**.
- Solutions of salt of weak acid and weak base are called **simple buffers**. e.g., $\text{CH}_3\text{COONH}_4$
- A weak acid together with a salt of the same acid with a strong base are called **acid buffers**. e.g. $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
- A weak base and its salt with a strong acid are called **basic buffers**. e.g. $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

is known as **Henderson's equation** and enables the calculation of pH values of buffer solutions made by mixing known concentrations of a weak acid and its salt.

- The phenomenon of the interaction of anions and cations of the salt with the H^+ and OH^- ions furnished by water yielding acidic or alkaline or sometimes even neutral solution is known as **salt hydrolysis**.
- Salts of strong acids and bases do not undergo hydrolysis e.g., KCl .
- A buffer solution is assumed to be destroyed if an addition of strong acid or base, changes

its pH by 1 unit i.e. $\text{pH} (\text{new}) = \text{p}K_a \pm 1$. This means the ratio $\frac{[\text{Salt}]}{[\text{Acid}]}$ or $\frac{[\text{Salt}]}{[\text{Base}]} = 10$ or $\frac{1}{10}$.

- The aqueous solution of the salt of a weak acid and a strong base is alkaline because of hydrolysis.
- The aqueous solution of the salt of weak base and strong acid is acidic because of hydrolysis.
- The reaction of an anion or cation with water accompanied by cleavage of O—H bond is called **hydrolysis**.
- **Degree of hydrolysis** is defined as the fraction of the total salt that has undergone hydrolysis on the attainment of the equilibrium.
- The **hydrolysis constant** K_h of the salt varies inversely with the dissociation constant K_a of the weak acid. $K_h = K_w / K_a$
- Weaker the acid, the greater is the hydrolysis constant of the salt.
- The pH of a salt of a strong acid and strong base is 7 and the solution is neutral e.g., NaCl , KCl .
- The pH of a salt of a weak acid and strong base can be calculated using the relation:

$$\text{pH} = 7 + \frac{1}{2} [\text{p}K_a + \log C]$$

e.g., CH_3COONa , Na_3PO_4

- The pH of salt of weak bases and strong acids can be calculated by using the relation:

$$\text{pH} = 7 - \frac{1}{2} [\text{p}K_b - \log C] \quad \text{e.g., } \text{NH}_4\text{Cl}, \text{CuSO}_4$$

- The pH of a salt of a weak acid and weak base is given by

$$\text{At } 25^\circ\text{C, pH} = 7 + \frac{1}{2} [\text{p}K_a - \text{p}K_b]$$

e.g., $\text{CH}_3\text{COONH}_4$, AlPO_4

- For salts of weak bases and strong acids, degree of hydrolysis is given as

$$h = \sqrt{\frac{K_w}{K_b \times C}}$$

- For salts of weak acids and weak bases, the degree of hydrolysis is given as

$$h = \frac{K_w}{K_a K_b}$$



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